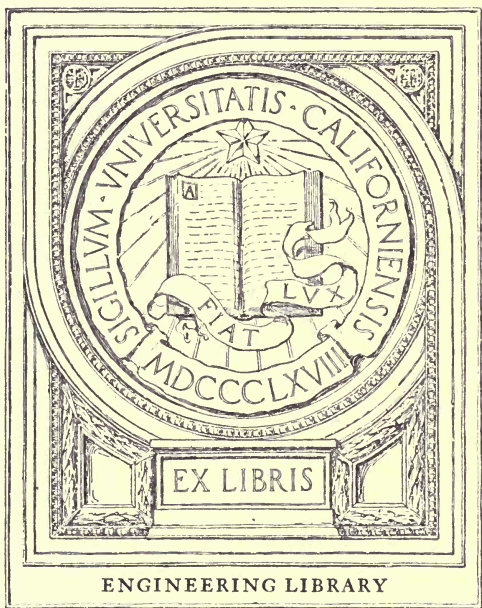


# HEAT

W. J. R. CALVERT

HORATIO WARD STEBBINS

1878-1933



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HORATIO WARD STEBBINS received the A.B. degree at the University of California in 1899, and the B.S. degree at the Massachusetts Institute of Technology in 1902. After twelve years of professional practice he entered the Department of Mechanical Engineering at Leland Stanford Jr. University where he became Associate Professor. He was a member of the American Society of Mechanical Engineers, Sigma Xi, and Phi Beta Kappa. He was an ardent student and a beloved teacher. This book is given in memory of him.







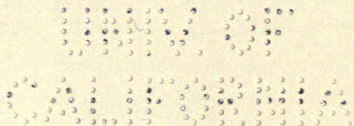
# HEAT

BY

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ANNALS  
IN MEMORIAM

Horatio Ward Stebbins

## PREFACE

The book is divided into two parts. The first Part is intended to cover the ground of a general school education ; that is to say, it carries the work rather beyond the standard of the School Certificate or the Army Entrance Examination. Several of the chapters have a supplement in smaller type, which can be omitted without disturbing the continuity of the treatment : it is intended that they should be omitted by those who are still at the general education stage. The second Part, also in the same smaller type, is intended for those who are making Heat a main subject ; it brings the work up to University Scholarship standard, and so is ample for such purposes as the Higher Certificate or the Intermediate B.Sc.

In determining the treatment to be adopted in Part I, I was guided by a consideration which is sometimes overlooked. Of those who begin the study of Heat, a fair proportion will not carry their work much beyond this elementary stage : the subject will merely form part of their general education. While, therefore, the treatment must form a foundation upon which a systematic study can be built up, it cannot be regarded as a foundation only ; it must, as far as possible, give some indication of the scope and aims of the subject, and the kind of problems with which it deals. If the treatment does not do this, one has been responsible for sending out into the world a number of "educated" people with quite erroneous ideas. Even more heavy is one's responsibility to those who begin with an open mind and have not yet discovered in what direction their interest and aptitude lie ; in the elementary portion of the subject one is supplying them with a large portion of the material

upon which they must base their decision when the time comes for them to make it.

I have assumed that the majority of those who begin the subject will have little or no interest in the determination of coefficients of expansion or specific heats unless it is made clear to them, at the outset, that objectives which appear to them reasonable cannot be reached without dealing with such measurements. In one of J. B. Biot's works there occurs a sentence which has always appealed to me as extraordinarily appropriate. "Toutes ces choses ne peuvent se déterminer sûrement que par des mesures précises que nous chercherons plus tard ; mais auparavant il fallait au moins sentir le besoin de les chercher."

I have also rather emphasised the practical applications because at this stage the concrete usually has a stronger appeal than the abstract. At the same time I have tried to keep attention fixed upon the underlying principles, and have not shirked reasonable difficulties : the book is not intended to be "Science made easy," and my experience is that most beginners are prepared to make serious effort (or at any rate can be induced to do so) if they are satisfied that their efforts lead to a reasonable end. In any case there is no Royal Road to success.

One or two points in the treatment of the book as a whole may be mentioned. In all experimental work special attention is directed to the degree of accuracy to which the work is likely to attain. One of the objects of a scientific training is the realisation that in the search for truth the ultimate appeal is to experiment ; but this realisation can hardly be expected to come to those who carry out operations without any idea of the extent to which their results can be trusted. For example, suppose a beginner carries out an "experiment" to verify some physical law, and does not know the precise limitations of his apparatus and method. If the results come out (by accident) more or less as he hopes or expects he is apt to say that he has verified the law ; if they do not, he may take refuge in the statement that if the



apparatus had been "more accurate" the results would have verified the law. This is appeal to the text-book, not to experiment, and is the reverse of scientific training; it might possibly be suitable preparation for a successful political propagandist. It is true that any one who has learnt to have a (justifiable) confidence in his own experimental work and to weigh evidence, has already achieved considerable development; but the sooner he begins to learn the better.

In the same way I have tried, wherever possible, not to speak of any effect without giving some idea of its magnitude. It can only cause unnecessary confusion to a beginner if he reads a statement that vapours near their saturation points do not obey the gas laws and then finds that in calculations on the chemical hygrometer (quite possibly the only calculations of this type which he meets) it is tacitly assumed that they do. A sense of proportion is another useful result of a genuine scientific training.

I have thought it worth while, even in so elementary a book, to give references to original papers: no doubt comparatively few readers will look them up, but those who do will gain a great deal. Even those who do not will at least be able to use the dates to get some idea of the chronological development of the subject. Perhaps also it is a check on the writer; the fact that the source of information is given and that he has read these papers may help to carry conviction that he is describing experiments which have been done and not things which might have been but were not.

I have also thought it worth while to give details and dimensions in the case of many experiments of the laboratory or lecture type; such details may possibly be of use in saving time for those who are arranging a course and are not able to give as much time as they would like to preliminary experiment. In any case the information can do no harm and is some guarantee that all the work has actually been carried out. Many of them are the outcome of experiments which I have made for my own information in an examination of the degree of accuracy of certain familiar operations.

It is hardly necessary at the present day to make any comment on the use of very simple calculus in Part II; I do not anticipate that many readers will find it a source of trouble. It is true that something is to be said for the very cumbrous treatment which avoids it, but life is short; it is conceivable that a clearer insight into the ideas of addition and subtraction might result from the use of a swan pan in the early stages of arithmetic, but I have not seen any suggestion for its revival.

In conclusion I should like to express my gratitude to Mr. Archer Vassall for his interest in this book and his very great help, especially in giving me the benefit of his unrivalled gift for detecting whether a particular presentation of a subject will appeal to certain types of mind or not; to Mr. Parsons, of the Physical Laboratories, who has made a good deal of the apparatus described, and last but not least to many Harrovians past and present, who have been concerned with me in the study of this subject.

W. J. R. C.

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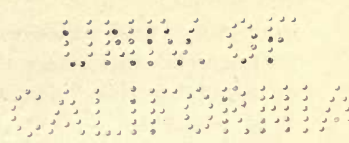
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## PART I

### CHAPTER I

#### INTRODUCTORY

If we place our hands on a wall upon which the sun has been shining on a summer's day, we are conscious of a sensation which we express by saying that the wall feels "hot"; if we pick up a lump of ice, or a frog, we are conscious of a sensation which we express by saying that the ice (or the frog) feels "cold."

Now it is not possible to put into words what we mean by any particular sensation (let the student who doubts this try to think how he would explain to a man blind from birth what he means when he says that an object is green; or to a hard-working charwoman the particular joy of a really long drive at golf or the ascent of a difficult bit of rock); but if we try to consider why the wall feels hot or the frog cold we find that another idea comes in. For example, when one gets into a hot bath, not only is one conscious that the water is "hot," but one has a feeling that something is passing from the water to oneself which makes one feel warm. To this "something" we give the name heat, and we try to get a mental picture of what is going on by saying that the water feels hot because when we get into it heat passes from the water to us.

This idea of heat as something which can be communicated is brought out more definitely if we consider the case of a gas-ring. We are quite clear that the flame of the gas-ring is not getting hotter, but we know that if we put a

saucepan of cold water on the ring the water will get steadily hotter until ultimately it boils. The gas-ring then can go on supplying this "something" which we call heat as long as it is alight.

We have here two distinct ideas: one that an object may be in a certain state which we call "hot" or "cold"; the other that when an object becomes hotter something which we call heat is communicated to it. Following up these ideas we then go on to say that an object feels hot because it can communicate heat to us when we touch it. It should be noted that this last sentence is not a definition of the condition of hotness; the idea of hotness came first as a result of a sensation, and the idea of heat was developed in an attempt to picture what was happening. This condition of an object is usually expressed in scientific work as its temperature; a hot object is said to be at a high temperature and a cold one at a low temperature. These terms will be dealt with more fully in the next chapter, while the nature of heat is considered in Chapters VII and VIII. At the moment it will be convenient to notice some of the effects of heat, and then some of its sources.

**Effects of Heat.**—1. One of the most common effects of heat on a substance is that a change in size takes place. In nearly every case a substance when heated expands;<sup>1</sup> this expansion may be illustrated by the following simple experiments.

In Fig. 1, D represents a metal rod or tube (a piece of iron gas-pipe answers very well) 6 or 8 feet long. This is carried on two supports F, G. One end of the rod is prevented from moving by means of a heavy weight, while the other end is in contact with a small block of wood B, placed in alignment with two similar blocks A and C. The rod is heated by means of half a dozen burners, and when it is hot

<sup>1</sup> Water between 0° C. and 4° C. contracts when heated; some specimens of invar (Chapter IV) contract slightly. A piece of india-rubber stretched by a weight appears to contract on heating, but this is an indirect effect as a greater force is required to stretch the india-rubber when warm than when cold.

it will be seen that B is pushed out about  $\frac{1}{8}$  to  $\frac{1}{4}$  inch beyond the alignment of A and C. If the rod is allowed to cool it

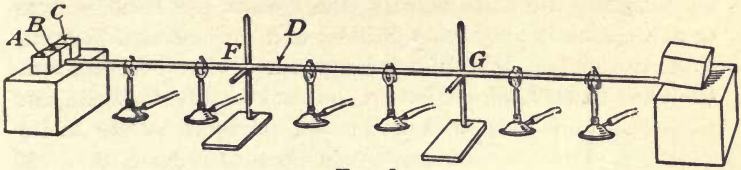


FIG. 1.

returns to its original length, leaving a gap between its end and the block B.

To illustrate the expansion of a liquid a flask is taken and fitted with a cork through which passes a narrow glass tube. The flask is completely filled with water (which may be coloured by adding to it ink or a little aniline blue to make it more easily seen) so that the liquid stands a little way up the tube. A piece of paper is placed behind the tube and a mark is made at the surface of the water (Fig. 2). On heating the flask, the water at first sinks a little. This is because the flask gets hot before the water, and as the glass expands the capacity of the flask increases and so the water-level sinks. In a short time, however, the water-level will be seen to rise above the mark and may ultimately reach the top of the tube; for when the water is heated it expands more than the glass.

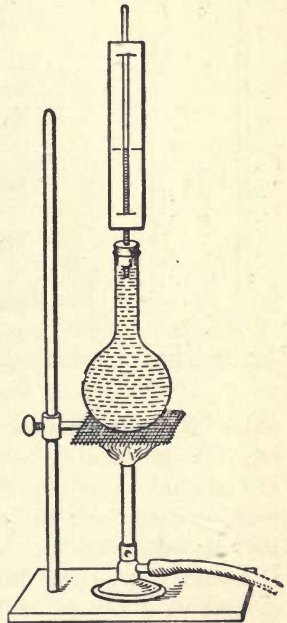


FIG. 2.

To illustrate the expansion of a gas a flask and tube similar to that of the last experiment is taken, but the flask is simply

filled with air. It is inverted so that the end of the tube dips under the surface of some water in a bowl (Fig. 3). On warming the flask slightly (the heat of the hand is sufficient), the air expands and bubbles of it may be seen escaping from the end of the tube through the water. On allowing the flask to cool the air left in the flask contracts again, and

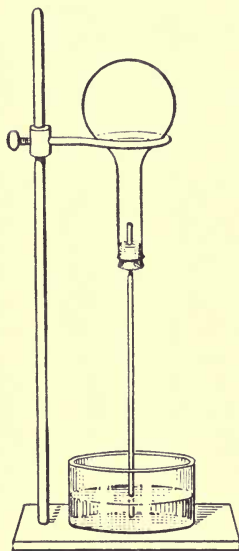


FIG. 3.

the water will be seen to rise in the tube, driven up by the pressure of the atmosphere on the water in the bowl.

In general solids expand a little, liquids more,<sup>1</sup> and gases very much more when heated through the same range of temperature.

Other effects of heat are—

2. A change of state may occur, e.g. ice may be turned to water or water to steam.

3. In general, but not always, a rise in temperature is caused.

These two effects are dealt with in Chapters IX and X.

4. An effect of heat of which use is made in the thermopile may be noticed here. If two dissimilar metals are joined together at one end and the other ends are in metallic connection

either through another wire, or directly, then on warming the junction a small electric current will flow round the circuit. This may be illustrated by taking two pieces of wire, one iron and the other copper (ordinary 22-gauge connecting wire does very well), soldering them together at one end and connecting the free ends to a sensitive<sup>2</sup> mirror

<sup>1</sup> An exception is the case of a liquid very near the critical point, where the expansion is in some cases greater than that of the gas (*see* Chapter XVII).

<sup>2</sup> The instrument used by the writer for this purpose and for use with a thermopile is a Paul mirror galvanometer resistance 8.75 ohms and sensitivity 10 mm. at 1 metre from the mirror for 1 micro-ampère.



galvanometer. On heating the soldered junction with the flame of a match, a decided deflection of the galvanometer will be obtained, indicating that a current is passing. This effect is greater with some pairs of metals than others; antimony and bismuth form a good pair, so do platinum and rhodium.

The thermopile is an instrument in which a number of small bars of two metals (nearly always antimony and bismuth) are joined in series. They are imbedded in an insulating material (pitch) with one set of junctions projecting at one end and the other set at the other.

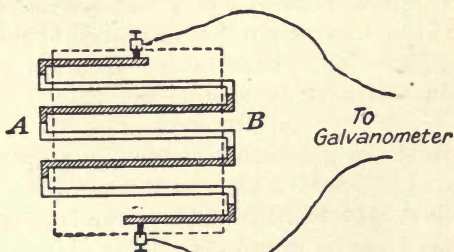


FIG. 4.

Fig. 4 shows only three junctions at each end; a usual number is sixteen or twenty-five arranged in four or five rows. A cap is placed over one end of the instrument covering one set of junctions B; on bringing a warm object near the other face a deflection of the galvanometer is obtained. If A is covered by the cap, and B exposed to the warm object, the current flows in the opposite direction. It does not matter which face is exposed so long as the other is covered, unless it is desired that the deflection of the galvanometer should be in one direction rather than the other. With a good galvanometer the thermopile forms a very sensitive instrument.

**Sources of Heat.**—The following sources of heat may be mentioned—

1. The sun.

2. Mechanical action, such as friction, percussion, compression.

3. Chemical action, e.g. combustion, explosion.

4. Electrical action, e.g. electric radiators, incandescent lamps.

5. Internal heat of the earth.

6. Radio-activity.

7. Physical change of state (see Chapters IX and X).

1 and 3 are outside the scope of this book.

2. *Mechanical Action*.—A simple experiment to illustrate the production of heat by friction is to take a drawing-pin and stick it into the end of a cork which serves as a handle. The head of the drawing pin is then rubbed briskly on a piece of blotting paper laid on the table. In a few moments the drawing pin will have become so hot that it is painful to touch.

To illustrate the production of heat by percussion, take a small piece of lead with a piece of thread or silk attached to it by which it may be lifted. Place the lead on a sheet of blotting paper laid on the top of a large weight which serves as an anvil. Strike the lead vigorously several times with a hammer. On holding the lead (by means of its thread) near a thermopile a deflection of the galvanometer shows that the lead has become hot: this will also be evident on touching the lead. In the absence of blotting paper the lead would communicate heat so quickly to the iron weight that very little effect would be obtained.

The production of heat by compression will be familiar to any one who has pumped up a bicycle tyre; it can be shown more strikingly by the old-fashioned toy known as the "fire syringe." This is a stout glass tube closed at one end and fitted with a well-fitting piston. To the underside of the piston is attached a small piece of cotton wool soaked in carbon di-sulphide, a very inflammable substance. The piston is inserted and then driven smartly down. The heat developed by the compression of the air causes the carbon di-sulphide to burst into flame.

4. *Electrical Action.*—This may be illustrated by connecting two or three inches of thin (No. 40 S.W.G.) copper wire to a few (say three) accumulators. The copper wire will be seen to become red hot, and by using more cells the wire can be fused.

5. *Internal Heat of the Earth.*—It is found that below the surface of the earth the temperature increases with the depth ; it is notably warmer at the bottom of a deep mine than at the surface. The increase of temperature with depth varies considerably ; the rough figure of  $1^{\circ}$  F. per 60 or 70 feet gives some idea of the amount. The interior of the earth near the centre must be very hot. It is possible that some part of this effect is connected with No. 6.

6. *Radio-activity.*—The radio-active substances, such as radium, are constantly undergoing change into other substances ; in the course of this change they give out certain types of electrical radiation and may give out an appreciable amount of heat.<sup>1</sup> Thus a very small quantity of radium bromide is able to maintain itself appreciably hotter (two or three degrees) than its surroundings. A given quantity of radium would be half transformed in something like 2,000 years and this remainder would be half transformed in another 2,000 years, and so on. During all this time heat is being developed.

<sup>1</sup> Owing to absorption of some of the radiation in the material itself (see Chapter VIII, "Relation of Heat and Work").

## CHAPTER II

### TEMPERATURE AND THERMOMETRY

It was pointed out in the last chapter that an object might be in the condition known as "hot" or "cold," these terms meaning that certain sensations would be experienced if the object were touched; and that this condition was referred to in scientific work as the temperature of the body. When we speak of a body at a high temperature, however, we imply something more than saying that it is hot; we imply that there is some standard of comparison, so that we can say quite definitely that one object is hotter than another, and that we can state the degree of hotness referred to some scale. We must now consider how this more complete idea is obtained.

As long as we are dealing with the same substance, our sense of touch will furnish us with a rough estimate of degrees of hotness. Thus in the case of water, we speak of it as cold, tepid, warm or hot, and these terms have some significance.<sup>1</sup> But when we deal with different substances the sense of touch is altogether unreliable. For example, if we take a piece of wood and a piece of iron and leave them on the ground on a winter's day, we shall find that the iron will feel colder than the wood. On the other hand, if we put the iron and the wood into a hot oven for some time, we shall find that the iron feels hotter than the wood. The reason for this is that an object feels hot or cold according

<sup>1</sup> The sense of touch is not always to be relied upon. Liquid air is very cold and red-hot iron is very hot, but the effect of these two things on the hand is somewhat similar; bad blisters and much pain resulting. Inexperienced people have been known to say that liquid air had "burnt" them.



to whether it heats or cools our hand when we touch it, and we estimate the hotness or coldness by the rate at which it does this, or as we have already expressed the matter, by the rate at which heat passes into or out of our hand. This rate depends on two things, first how hot the body is, and secondly on whether it is a good conductor of heat, i.e. whether heat can flow through it readily or not. Now it happens that iron is a much better conductor of heat than wood (see Chapter XII) ; so when we touch the iron from the oven, it is able to heat the hand more rapidly than the wood can and so feels hotter ; when the wood and iron are cold, the iron as the better conductor is able to cool the hand more rapidly than the wood can, and so feels colder.

There is, however, a perfectly definite test we can apply. If we put a red-hot iron bar into a dish of cold water, we know that the iron cools down, and the water becomes warmer ; if, however, the iron bar, instead of being made hot, had been left in a room beside the dish of water, then on putting the iron into the water we could not detect any change in either of them, whether we use our sense of touch or one of the artificially sensitive instruments described below. We can take this as our test and say that—If when two bodies are placed in contact neither of them becomes hotter or colder than it was before these two bodies were at the same temperature.<sup>1</sup> If one of them becomes colder, and the other warmer, they were at different temperatures.

### Thermometry.

Such a test is seldom convenient to carry out in practice, and it only tells us whether two bodies are or are not at the same temperature. In order to detect differences of tem-

<sup>1</sup> This only applies if there is no chemical action between them ; if strong sulphuric acid is added to water, both being at the same temperature as registered by a thermometer, the mixture will be much hotter than the constituents as heat is developed by the chemical action of the acid and water.

perature and express it on some scale an instrument called a thermometer is required. In constructing thermometers, use is made of one of the effects of heat, and the one most commonly used is the expansion of a liquid such as mercury or alcohol.

**To Construct a Simple Thermometer.**—The thermometer when finished will consist of a thick-walled tube of narrow bore, terminating at one end in a bulb. The bulb and part of the stem are filled with mercury or amyl alcohol ;

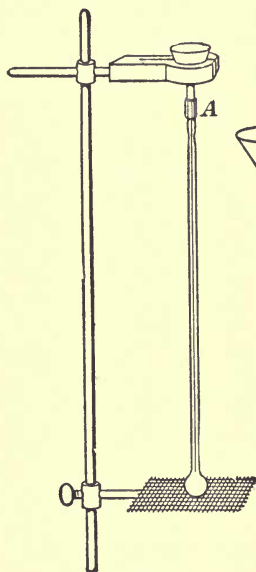


FIG. 5.

if alcohol is used it must be coloured, e.g. by a little cochineal. The tube is sealed at the top, and the space above the liquid is free from air. If the bulb be placed in warm water, the liquid will be heated up until the water and the liquid are at the same temperature. The liquid will consequently expand and will rise in the tube, and since this is of narrow bore, a small expansion will result in a considerable rise of the liquid. The final position will depend on the temperature of the water, and will thus give us some means of estimating how hot the water is.

A piece of thick-walled narrow-bored tubing is selected and a length of about 12 inches is cut off. One end of this length is sealed and a bulb of suitable size is blown. The tubing is then drawn out slightly close to the open end so as to form a constriction. A small funnel is attached to the open end by a piece of rubber tubing A, and the whole suspended from a stand as shown in Fig. 5. Some of the liquid

to be used, either mercury <sup>1</sup> or amyl alcohol is placed in the funnel; it will not run down into the bulb owing to the narrowness of the tube. The bulb is gently warmed by means of a burner, and the air in it expands, bubbles escaping through the liquid in the funnel. The heating must be gentle, otherwise the escaping air is apt to eject most of the liquid from the funnel. The bulb is then allowed to cool, and as the air contracts some of the liquid runs down the tube and into the bulb; it may be necessary to cool the bulb by immersing it in a beaker of cold water, and this is quite safe if the previous heating has not been carried far. The process is then repeated, taking care to dry the outside of the bulb before heating; in this way the bulb is about three-quarters filled with liquid.

It is not, however, possible to get rid of all the air in this way and the final stage of the filling is done as follows. Any remaining liquid in the funnel is emptied out, and the bulb is then heated so that the liquid in it boils. The vapour from the boiling liquid drives out the air and fills the space above the liquid. The boiling is continued until the vapour has been issuing from the funnel for some time, then the funnel is filled up with more liquid and the heating stopped. As the vapour in the bulb and tube cools, it condenses, and the liquid rushes in and fills up the tube and bulb. Care is necessary to see that there is sufficient liquid in the funnel to fill the bulb and tube, otherwise air will follow the liquid and the whole process will have to be done again. It is not always easy to get rid of the last traces of air, a small bubble being very apt to form just under the shoulder where the tube and bulb join. This bubble can sometimes be got into the tube by taking the thermometer in the hand, holding it

<sup>1</sup> Mercury should not be used by beginners, as its boiling point is so high that accidents to the tube are rather likely to happen, and moreover mercury vapour is not healthy. Amyl alcohol is selected as having a boiling point higher than that of water, but not so high as to involve intense heating. The vapour of amyl alcohol has a most unpleasant effect on the throat and so should not be inhaled unnecessarily.

by the tube just above the bulb, the upper end of the tube lying along the forearm, and swinging it to and fro with a stiff arm. The liquid being heavier than the bubble tends to get as far away as possible from the point about which it is swung and hence the bubble is displaced up the tube. Once there, a little judicious warming may get it above the constriction into the funnel where it can escape.

We have now got the bulb and tube full and the next thing to do is to adjust the quantity of liquid so that it will stand at the proper height in the tube. This will obviously depend upon what sort of temperature the thermometer is intended to register. In this case we shall adopt an arrangement very often met with and make our thermometer capable of registering temperatures up to, and a little above, the boiling-point of water. The thermometer when finished will be sealed off at the constriction; we must therefore adjust the amount of liquid so that when the thermometer is in boiling water, the level of the liquid will be a little below this point (about an inch and a half). Remove the funnel and place the thermometer in boiling water. The liquid expands, and as it oozes out of the open end of the tube it is wiped off. Now remove the thermometer, dry the outside and then warm it over a flame and drive out a little more of the liquid. Now replace the thermometer in boiling water and see whether the liquid stands at the proper height below the constriction. If it does, we can proceed to the next process, i.e. sealing off.

A blowpipe is prepared and the thermometer is once more dried and heated until the liquid has expanded beyond the constriction. It is then allowed to cool and the liquid carefully watched. As soon as it has passed back through the constriction the blowpipe flame is at once directed on this spot, the end of the tube drawn off and the sealing of the tube completed. The thermometer should be set aside for a few days before anything more is done to it, as the glass after heating does not return to its normal size and condition for some time.



We have now got an instrument which will enable us to say whether two objects are at the same temperature or not. For if we put it in contact with one of them, it will be heated or cooled until it is at the same temperature as the object; the liquid will expand or contract until the surface is in a certain position. If it is put in contact with the other, and the liquid comes to the same position, the two objects are at the same temperature.<sup>1</sup> In order that the indications of the instrument may have some definite meaning it must be graduated. For this purpose we must determine the position of the liquid when the instrument is at two temperatures agreed upon as standards. These two positions are called the "fixed points" of the thermometer. The temperatures are the temperature at which pure ice melts and the temperature at which pure water boils under standard atmospheric pressure, i.e. when the barometer stands at a height of 760 mm. or 29.9 inches. (It is found that the boiling-point of any liquid varies with the pressure; see Chapter X.) These two points are called the lower fixed point and the upper fixed point respectively. The interval between the fixed points is divided into a number of equal parts called degrees, and the whole then forms a scale of temperature. There are three scales of temperature in general use. That used in almost all scientific work and for ordinary use on the Continent (except the Scandinavian countries) is called the centigrade scale. The interval between the fixed points is divided into one hundred degrees; the lower fixed point is called  $0^{\circ}\text{C}$ . (nought degrees centigrade) and the upper  $100^{\circ}\text{C}$ . (one hundred degrees centigrade). The scale used in England for ordinary non-scientific work is called the Fahrenheit scale, after its originator. It is the oldest of the three scales. On this, the interval between the fixed points is divided into 180 degrees, but the lower fixed point is not taken as 0 but 32, so that the upper fixed point is therefore

<sup>1</sup> This is not a self-evident proposition. It depends on the *experimental fact* that if two substances separately pass the test of equality of temperature (given on page 9) with a third, they will pass this test of equality with one another when put in contact.



212° F. The zero of this scale is therefore 32 degrees Fahrenheit below the lower fixed point or freezing point. The third scale, known as the Réaumur scale, is in less common use, but is met with in the Scandinavian countries. The interval between the fixed points is divided into 80 degrees; the lower fixed point is called 0° R. and the upper 80° R.

Thus in all three scales the fixed points represent the same temperatures, but the interval is divided up differently, and different numbers are assigned to the fixed points.

**Determination of the Lower Fixed Point.**—A large funnel is taken and filled with small pieces of clean ice.<sup>1</sup>

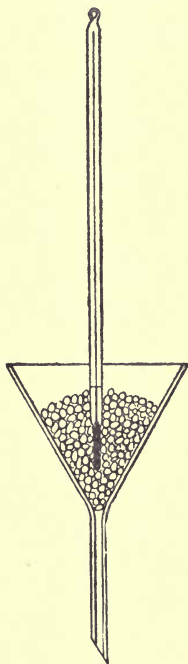


FIG. 6.

Underneath the funnel is placed a dish to catch the water which drains away as the ice melts. The bulb of the thermometer is immersed in the ice, which is packed round it, as in Fig. 6, and heaped up to such a height that when the liquid has ceased contracting it is just visible above the ice. A little distilled water is poured over the ice to wash it, and the apparatus left for a considerable time, say half an hour. A fine scratch is made in the glass (by means of a file) at the level of the liquid. The apparatus is then left for a further period and then inspected again to see that the position of the surface of the liquid is still at the mark. If it is, this may be taken as the lower fixed point. If it is not, a new mark must be made, and tested by leaving the apparatus for a further period to see if the liquid remains there. The mark must not be taken as the lower fixed point until it satisfies this test.

<sup>1</sup> The ice must be clean, as the melting point is affected by soluble impurities. It is also desirable that the water formed should be able to drain away, although this point is sometimes disputed, but see page 133, Chapter IX.

**Determination of the Upper Fixed Point.**—To determine the upper fixed point the thermometer must be suspended in the steam<sup>1</sup> of boiling water, and the apparatus employed for this purpose is known as a hypsometer (Fig. 7). It consists of a cylindrical metal vessel A to serve as a boiler, surmounted by a tube C open at the top. C is surrounded by a wider tube, with an outlet B on one side and a glass U tube D containing water to serve as a manometer or pressure gauge. The wider tube is provided with a lid, which has an opening at the centre closed by a cork through which passes the thermometer. A contains water which is boiled, and the steam passes up C, then down the wider tube and escapes from the outlet. The thermometer must hang in the steam and the bulb must not touch the water nor be near enough to it to be splashed. It must be so far down that when the surface of the liquid comes to its final position, it is just visible above the cork. The water in the two limbs of D must stand at the same level; when this is the case the pressure of the steam is the same as that of the atmosphere. If the water is boiled too rapidly the steam cannot escape fast enough from B and the gauge D shows an increase of pressure. This must be remedied by heating less strongly.

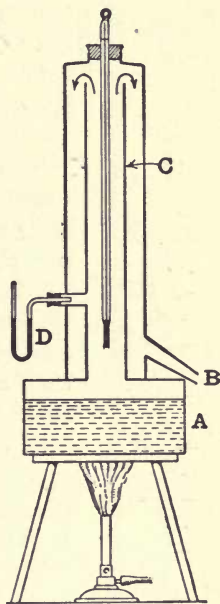


FIG. 7.

When the steam has been issuing freely for some time, say twenty minutes, a mark is made at the surface of the liquid in the thermometer. The reading of the barometer

<sup>1</sup> The temperature of the water may be above the true boiling point for pure water if there are any impurities, and even if there are not the temperature of the water may be too high (see Chapter X, page 160).

is taken, and if this is not 760 mm. a correction must be applied by means of the tables showing vapour pressures. The mark is tested as in the case of the lower fixed point by leaving the apparatus for some time and seeing that the liquid is still in the same position. Having determined the two fixed points, we can now graduate the thermometer.

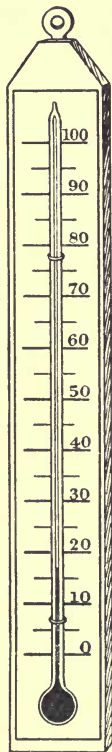


FIG. 8.

If we decide to graduate our thermometer on centigrade scale, we can take a strip of paper and mark off on it a distance equal to that between the two marks we have made on the tube. We can then divide up this distance into 100 equal parts, and number them from  $0^{\circ}$  to  $100^{\circ}$  C.

To mount the thermometer, a strip of wood is taken about 2 inches wide and a little longer than the thermometer. A hole is made to admit the bulb. The thermometer is laid on the wood and the paper scale adjusted behind it so that the 0 comes opposite the lower fixed point and the 100 opposite the upper. The whole is then fixed in position by drilling two pairs of small holes through the scale and wood on either side of the tube and passing pieces of wire round the tube, through the holes, and twisting them up tightly at the back. The final product appears as shown in Fig. 8.

This thermometer is easy to make, and is quite suitable for some purposes. It has, however, certain serious disadvantages. The paper scale prevents it from being put into liquids; it is large, which makes it cumbersome and, what is worse, makes it take an appreciable quantity of heat from any hot object with which it is put in contact, so that the final temperature recorded by the thermometer is not the original temperature of the object. Moreover it requires a considerable time for the liquid to be heated up owing to

the bulb being a sphere the surface of which is smaller in comparison to the volume than that of any other shaped object, and alcohol is a bad conductor of heat. For these reasons a modified form is generally used the thermometer is smaller, the bulb is cylindrical instead of spherical, and the liquid is almost always mercury.

One type of thermometer is shown in Fig. 9. It consists of a thin tube A, terminating in a cylindrical bulb. A wider tube B sealed on to the bulb as shown, serves to protect the thermometer tube and to contain the scale which is engraved on a flat piece of milk glass C. In some forms the upper end of inner tube is sealed in position by three small pieces of glass D; in others, the attachment of the scale to the tube (by means of two small pieces of wire in much the same manner as in our simple thermometer) gives it sufficient lateral support, since the scale fits tightly into the outer tube. Thermometers of this type are usually fairly cheap and the scale is easily read and is protected from any liquids in which the thermometer may be immersed. Very cheap types are supplied with paper scales, but these are not so satisfactory. This type, known as the "sleeve" pattern, is of German origin.

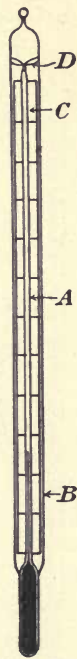


FIG. 9.

Another type of thermometer is shown in Fig. 10. Thermometers for accurate work are always of this type and not of the sleeve pattern. It consists of a thick-walled tube of very narrow bore, terminating in a cylindrical bulb. The scale is etched on the surface of the tube itself, and in order to make this more visible, the back of the tube is made opalescent, or in some cases a strip of opalescent milk glass is worked into the tube when it is made, so that the section of the tube is as shown in Fig. 10. The bulb is blown separately and sealed on to the tube. Thermometers of this type are undoubtedly more suitable for accurate work, and are also

the only type which can be used for high temperature work (see below). They are also less liable to break. They are, however, more expensive than the sleeve pattern although cheap forms are to be obtained. These latter are usually not very satisfactory for general work; the scale is generally not so easy to read as in the sleeve pattern, and this trouble is often accentuated by the use of unsuitable material for marking the scale, which is attacked and dissolved by liquids such as alcohol, and so after a time only the actual etching is left and the scale becomes very difficult to read.

Mercury thermometers can be obtained reading up to  $400^{\circ}$  C. in spite of the fact that at ordinary pressures mercury boils at  $357^{\circ}$  C. This is done by making use of the fact that the boiling-point of a liquid is raised by pressure. The space above the liquid, instead of being vacuous, is filled with nitrogen under a pressure of three or four atmospheres. In order to leave sufficient room for this gas when the mercury rises nearly to the top of the tube, the upper part of the bore is enlarged to a small bulb, as shown in Fig. 11.

This arrangement is usually adopted even for low temperature thermometers as a safeguard against bursting the thermometer by accidental overheating; it



Milk Glass  
Section of Stem.

FIG. 10.



FIG. 11.

forms a small reservoir into which the mercury can flow.

### Thermometers for Special Purposes.

*The Clinical Thermometer.*—This thermometer is intended to read the temperature of the human body; the range therefore is small, usually from  $95^{\circ}$  F. to  $110^{\circ}$  F.,<sup>1</sup> and so the

<sup>1</sup> Fahrenheit, writing of the use of the thermometer to detect "fevers and other distempers," observes that it is sufficient for most cases to



stem can be short although the graduations show fifths of degrees. It is of the thick-walled type, but the special point is that the bore is very constricted at one point (Fig. 12). When the thermometer is used, the expanding mercury can force its way past the constriction, but when the thermometer is removed from the patient the mercury contracts, and the weight of the column above A is not sufficient to force it back through the constriction and so it stays where it is, indicating the temperature reached. It can thus be read at leisure. The mercury is forced back again for further use by shaking the thermometer sharply.

It will thus be seen that the clinical thermometer is a short range maximum thermometer. These thermometers are made in different sizes, known as "half minute," "one



FIG. 12.

minute," etc. This means that the quantity of mercury and the thickness of the glass is such that the time indicated gives some idea of the time required for the thermometer to take up the temperature of the patient. In practice, however, a half minute thermometer is usually allowed about one minute, a one minute is allowed two, and so on. These allowances are probably excessive under good conditions, but it is obviously better to err on that side as the thermometer should not indicate too high a temperature whatever time is allowed.

*Maximum and Minimum Thermometers.*—For some purposes, e.g. in meteorological work, it is necessary to know the highest or the lowest temperature recorded during a certain interval, say during the day or the night. Thermometers capable of indicating this are known as maximum

have a thermometer reading up to 120° F., "as I have seldom come across persons having a higher temperature than 120°." His experience must have been remarkable if he *ever* came across any one with a temperature anything like this, although there has been such a case recorded: the patient died.

thermometers or minimum thermometers respectively. One type of maximum thermometer is arranged as follows:—

A mercury thermometer is made with a horizontal stem. A small light index, shaped like a small bar bell and usually made of iron or glass, is placed in the tube. The index can slide freely along the tube. When the mercury expands, the surface of the liquid pushes the index before it. This is due to an effect known as surface tension, which makes a liquid behave as if the surface were formed of a sort of skin, so that a definite effort is needed to push an object through it (an example of this is the well-known trick of making a needle float on the surface of water). When the mercury contracts it leaves the index behind, so that the left hand end of the index shows the furthest position reached by the surface of

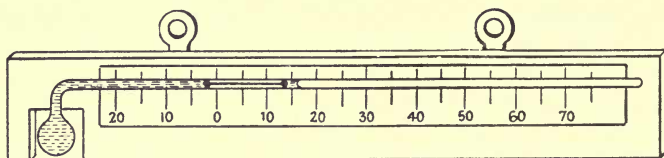


FIG. 13.

the mercury and so indicates the maximum temperature reached. The instrument is re-set by tilting the tube and causing the index to slide down to the surface of the mercury.

Much the same principle is employed in the minimum thermometer (Fig. 13). In this case the liquid used is alcohol and the index is immersed in the liquid. When the liquid expands it flows past the index (the ends of which do not fill up the tube), but when the liquid contracts and the surface reaches the index, it pushes it back rather than break the surface. The position of the right hand end of the index, therefore, represents the lowest temperature attained. The instrument is re-set by tilting up the left hand end of the tube so that the index slides down to the surface of the liquid. These instruments are known as Rutherford's maximum and minimum thermometer. For maximum thermometers

Rutherford's form is not very much used. A very usual form is Negretti's, which works on the same principle as the clinical.

*Six's Maximum and Minimum Thermometer.*—This is a combined maximum and minimum instrument. A (Fig. 14)

is the bulb of the thermometer, and its tube is bent as shown and terminates in a bulb B. A is filled with alcohol, which extends as far as E. The part E F is filled with mercury. The tube above F and part of the bulb B are filled with alcohol; the space above B being occupied by alcohol vapour. The part A E is the thermometer proper, so that we are using an alcohol thermometer. When the temperature rises the alcohol expands, pushing the column of mercury down in E and up in F. When the temperature falls the alcohol in A contracts and the pressure of the vapour in B drives the mercury column back. Scales are

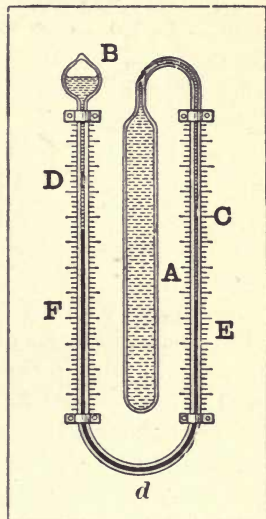


FIG. 14.

placed on each limb, giving the temperature from the position of F or E.<sup>1</sup> Above E and F are two small light steel indexes, provided with small springs capable of supporting them in the tube. When the temperature goes down, the end E of the mercury pushes up its index, while the other is left behind. When the temperature rises, the end F of the mercury column pushes its index up, while the other is left behind. Thus the lower end of the right hand index gives the minimum temperature, and the lower end of the left hand the maximum. The indexes are

<sup>1</sup> Since the mercury column itself expands the right hand scale divisions are not exactly equal to the corresponding divisions on the other scale.

reset by means of a small magnet. It should be noticed that the mercury column is there simply to move the indexes; the thermometric liquid is the alcohol in A. Six's thermometer is not suitable for accurate work, but is in much favour with gardeners.

**The Relation between the Three Scales of Temperature.**—We have seen that in each scale the two fixed points are the same, i.e. the melting-point of ice and the boiling-point of water under standard atmospheric pressure. In the Fahrenheit scale the interval between the fixed points is divided into  $180^\circ$ ; in the centigrade and Réaumur scales this interval is divided into  $100^\circ$  and  $80^\circ$  respectively. Thus a range of  $180^\circ$  F. = a range of  $100^\circ$  C. = a range of  $80^\circ$  R., or 9 Fahrenheit degrees = 5 centigrade degrees = 4 Réaumur degrees.

Now when we wish to express a temperature as measured on one scale, in terms of another, this relationship will enable us to do it. But in the case of the Fahrenheit scale the lower fixed point is called  $32^\circ$  not  $0^\circ$ ; so that the three scales do not all start from the same point. In converting scales from one temperature to another, the point to keep in mind is *how many degrees is the temperature above or below freezing-point.*

For example, let us express  $98^\circ$  F. in the centigrade scale.  
 $98^\circ$  F. =  $98 - 32$  or  $66^\circ$  above freezing-point.

9 Fahrenheit degrees = 5 centigrade degrees.

$66$  Fahrenheit degrees =  $\frac{5}{9} \times 66 = 36.6$  centigrade degrees.

$\therefore 98^\circ$  F. =  $36.6$  centigrade degrees above freezing-point.

=  $36.6^\circ$  C. (since freezing-point is  $0^\circ$  C.).

Again, suppose we wish to express a temperature of  $15^\circ$  C. on the Fahrenheit scale.

$15^\circ$  C. = 15 centigrade degrees above freezing-point.

$$= \frac{15 \times 9}{5}$$

= 27 Fahrenheit degrees above freezing-point.

But freezing-point =  $32^\circ$  F.

$\therefore 15^\circ$  C. =  $27 + 32 = 59^\circ$  F.

In dealing with conversions from centigrade to Réaumur and the reverse it is not necessary to consider this question of freezing-point since both scales start from the same point. Thus, to express a temperature of  $18^{\circ}\text{C}$ . on the Réaumur scale,

$$\begin{aligned} 5 \text{ centigrade degrees} &= 4 \text{ Réaumur degrees.} \\ 18^{\circ}\text{C.} &= \frac{4}{5} \times 18 = 14.4^{\circ}\text{R.} \end{aligned}$$

But whenever the Fahrenheit scale is involved, it is well worth while introducing the step of the number of degrees above freezing-point, otherwise the  $32^{\circ}$  is apt to be added or subtracted at the wrong stage, and a serious error introduced.

Temperatures below freezing-point are expressed on the centigrade and Réaumur scales by the use of the minus sign, thus  $-10^{\circ}\text{C.} = 10$  centigrade degrees below freezing-point. On the Fahrenheit scale in the same way, temperatures so low as to be below  $0^{\circ}\text{F}$ . are expressed by means of the minus sign. The conversion from one scale to the other is precisely the same whether the temperatures are below or above freezing-point.

Example.—Express  $10^{\circ}\text{F}$ . as a centigrade temperature.  
 $10^{\circ}\text{F.} = 32 - 10 = 22$  Fahrenheit degrees below freezing-point.

$$\begin{aligned} &= \frac{22 \times 5}{9} = 12.2 \text{ centigrade degrees below freezing-point.} \\ &= -12.2^{\circ}\text{C.} \end{aligned}$$

As another example, express  $-20^{\circ}\text{C}$ . on the Fahrenheit scale.

$-20^{\circ}\text{C.} = 20$  centigrade degrees below freezing-point.

$$= \frac{20 \times 9}{5}$$

$= 36$  Fahrenheit degrees below freezing-point.

$= 36$  Fahrenheit degrees below  $32^{\circ}\text{F}$ .

$= 32^{\circ} - 36^{\circ}$ .

$= -4^{\circ}\text{F}$ .

Of the three scales, that of Fahrenheit is the oldest, having been introduced by him about 1765; it was, in fact, the first satisfactory scale used. His idea was to avoid using the



minus sign, so he made a scale in which the lowest temperature he met with in his travels in Iceland should not come below zero. The actual value of the zero he took as the lowest temperature he could obtain with a mixture of ice and salt. He did not, in his earlier work, use the melting-point of ice and the boiling-point of water as fixed points and the value of the degree seems to have been based on various considerations.<sup>1</sup> He did, however, in the end use the two fixed points now adopted.

**Note on the Definition of Temperature.**—We have seen that temperature is a condition or state of a body, which we appreciate primarily by our senses. The test for whether two bodies are or are not at the same temperature is given by whether when they are placed in contact neither of them changes its condition. A very unsound, but frequently-encountered definition is “One body is said to be at a higher temperature than another, if, when they are placed in contact, heat passes from the first to the second.”

This is unsound because the idea of the existence of heat came as an attempt to picture what was happening to account for our sensation of hotness. It is probable that there is something corresponding to our conception of heat (as we shall see in Chapter VIII heat is a form of energy), but it is not directly perceptible to us; to introduce it in the definition of temperature is arguing in a circle or is meaningless. A more detailed consideration of scales of temperature will be met with later (see Chapter XVI, p. 253).

<sup>1</sup> One of his earlier scales made use of the human body temperature as a fixed point. In one of his later papers he mentions that a mixture of alcohol and water in the proportion of 4 : 1 expands  $\frac{1}{8000}$  of its volume at freezing point (of water) for each 1° of his scale and seems to imply that he made use of this fact in fixing his degrees. It is worth noticing that mercury expands almost exactly  $\frac{1}{8000}$  of its volume at 32° F. for each 1° F. rise in temperature, although this point is not mentioned in his papers.

### CHAPTER III

## EXPANSION OF SOLIDS

We have seen that most solids expand when heated ; this expansion is of great importance in practical life. In some cases it can be made to serve useful purposes, while in others it is a nuisance for which provision has to be made. There are two important points to be noticed in connection with this expansion. In the first place the force exerted during the expansion of a solid when heated, or during its contraction when cooled, is very great, and secondly it is found that different solids expand by different amounts when heated through the same range of temperature.

The great force exerted during expansion or contraction may be illustrated by means of the apparatus known as the "bar breaker." It consists of a stout iron rod A (Fig. 15),

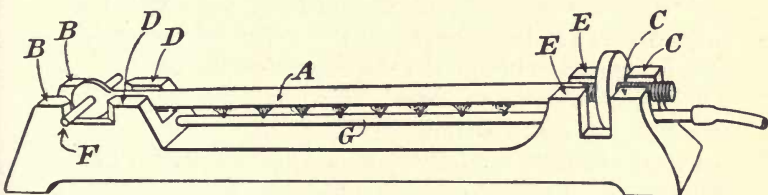


FIG. 15.

having near one end a hole large enough to admit easily a short bar of cast iron about  $\frac{3}{8}$ -inch diameter. On the other end of the rod is cut a strong screw thread on which a large nut works.

The rod is placed in a massive iron stand, so that the bar F rests against the stops BB. The faces of these stops are V-shaped so that the bar presses against two edges instead

of two flat surfaces, and the edge of the hole in A is V-shaped. The nut is turned as far as it will go, so that it presses against the stops CC. Thus A is prevented from expanding by the pressure of the bar F against the stops at one end, and the nut against the stops at the other. The gas burner G (a tube closed at one end and provided with a number of slits) is lighted, and as the rod gets hot the force it exerts is sufficient to snap the cast-iron bar.

The experiment may be varied so as to use the force of contraction. In this case the nut is screwed up against the stops EE, the cast-iron bar resting against DD. The rod is heated and as it expands the nut is screwed up against EE so as to take up the expansion. The rod is then allowed to cool, and the force it exerts in trying to contract to its former length breaks the bar as before.

The fact that different solids expand by different amounts under the same conditions may be illustrated in the following way. A strip of copper and of iron are securely riveted together. The two strips should be fairly thin and the rivets placed at intervals of about half an inch along each side. When the compound bar so formed is heated by a burner the copper expands more than the iron, and since it cannot slide over the iron without tearing away from the rivets it makes room for itself by bending the bar into a curve, the iron being on the inside and the copper on the outside. The bar is therefore seen to bend in this way when heated and to straighten again in cooling.

One of the most obvious cases in which expansion becomes a nuisance is the measurement of lengths by measuring rods or scales. The rod can only be correct at one particular temperature, and errors will be introduced unless all the measurements are taken when the temperature is at the particular value. This change in length of the measuring rods was a source of great difficulty in the earlier surveys of Great Britain, and it was in connection with them that much of the first systematic study of expansion was made.

In surveying a large area the process of triangulation is

adopted. In this process two points A and B are selected, and the distance between them carefully measured. This length AB is called the Base Line. A third point C visible both from A and from B is selected, and the angles CAB and CBA are measured by means of a theodolite. Knowing these two angles, and the length AB, the lengths CA and CB can be calculated. These are then used as the bases of two new triangles and the distance of two more points calculated. In this way the whole area is covered by a system of triangles, and it will be seen that the only length actually measured is that of the Base Line. Upon this measurement depends the accuracy of the whole survey.

In practice it is found desirable to have a base line of considerable length such as five or six miles, and as the accurate measurement of such a length is an affair of months, considerable variations in temperature are likely to take place while it is being carried out. Unless, therefore, the changes in length of the measuring rods have been studied in detail accurate surveying is impossible. For this reason, when General Roy made a survey of Hounslow Heath in 1784, upon which was founded the first Ordnance Survey of England, he had an apparatus designed for him by Ramsden and spent a considerable time investigating the behaviour of his measuring rods. Lavoisier and Laplace had made some very careful experiments on the same subject a few years before, but the account of them was not published until nearly twenty years later.<sup>1</sup> It is also worth mentioning that as early as 1754 John Smeaton had made a systematic study of the same subject, and although his experimental work cannot be considered as equal to these later experiments, it is valuable as the first really clear statement of the problem to be attacked and the difficulties to be overcome.

It was found that as far as could be determined with the apparatus used, if a given rod increased in length by a certain amount, say 1 mm. when heated from 10° C. to 20° C. as

<sup>1</sup> The French Revolution was not a time which was conducive to the pursuit and publication of scientific work.

measured by a mercury thermometer, it would expand a further 1 mm. when heated from 20° C. to 30° C., and so on. More accurate work has since shown that this is not strictly true for any substance, especially over a large range of temperature: but in most cases it is so nearly true that for moderate ranges of temperature it can be taken to be true for the great majority of practical purposes. To a fair degree of accuracy, therefore, we can say that a given rod increases in length by a certain amount for each degree rise in the temperature: the amount depends on the material of which the rod is made and obviously also on its original length.

If, instead of speaking of the rod expanding a certain amount per degree we say that it expands a certain fraction of its original length per degree, this fraction will depend only on the material. This, in practice, is done; since, however, the original length of the bar depends on the temperature at which it is measured some standard temperature must be agreed upon. It is usual to take the "original length" as the length at the temperature of melting ice. The fraction is called the *Coefficient of linear expansion* of the material. It is therefore defined as follows:—

**Definition of Coefficient of Linear Expansion.**—The coefficient of linear expansion of a substance is the fraction of its original length (measured at the temperature of melting ice) by which a bar of the substance would increase in length for each degree through which its temperature is raised.

Thus when we say that the coefficient of linear expansion of iron is .000012 we mean that a bar of iron 1 cm. long at 0° C. would expand .000012 cm. per degree; a bar 1 foot long at 0° C. would expand .000012 feet per degree; a bar 5 feet long at 0° C. would expand  $5 \times .000012$  feet per degree, and so on.

It may be noticed that the bar also increases in thickness, but since we are concerned only with linear expansion this does not affect the result; if we were concerned with the total change in volume we should speak of cubical or volume expansion instead of linear (see Chapters V and VI).



**Measurement of the Coefficient of Linear Expansion.**

We shall consider two laboratory methods of measurement. The first is rather rough and only suitable for giving approximate results; it is, however, quite satisfactory as far as it goes. The second is more accurate, being intended to give results trustworthy to 1 per cent.; it will be instructive to notice the much greater care and trouble involved in accurate work.

**Method I. For Approximate Results.**—This method is only suitable for metals. A tube of the given metal, about 60 cm. long and 0.5 cm. in diameter, has a mark made near each end. The distance between these marks is measured by means of an ordinary metre scale. The tube is clamped at one end, and at the other rests on a small roller carried by an arm attached to a rigid stand. The clamp is placed over one mark, while the roller touches the tube at the other. This roller is of known diameter, (usually 2 cms.), and to it is attached a pointer about 20 cm. long. A millimetre scale, fastened to a small block of wood, is placed on the bench just behind the pointer. The tube is connected by means

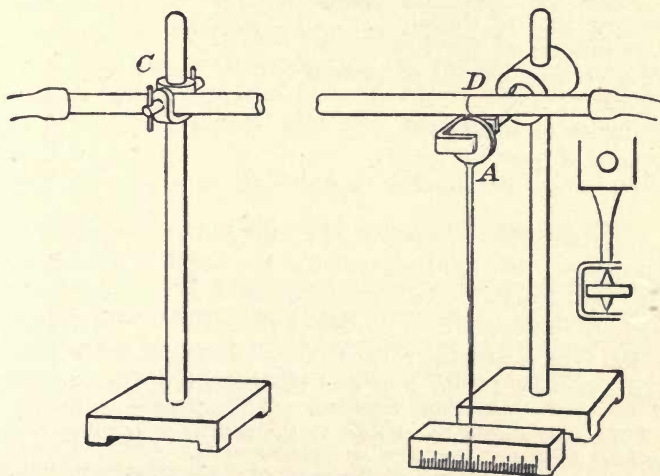


FIG. 16.

of a length of rubber tubing to a boiler from which steam can be supplied.

The metal tube CD is first allowed to take up the temperature of the room, which is determined by means of a thermometer, and the reading of the end of the pointer A noted : it is desirable to adjust the position of the scale so that the first position of the end of the pointer is exactly opposite a scale division.<sup>1</sup>

Steam is then passed through the tube ; as the latter expands the pointer moves over the scale. When no further movement takes place and the pointer has been at rest for two or three minutes, the reading of its extreme end is again noted. The tube is now removed, and the length of the pointer measured.

The following readings were obtained in a certain experiment and will be used to illustrate the method of obtaining the coefficient : it will be observed that the experiment happened to be done in a cold room.

#### Brass Tube.

Temperature of the air . . . . .	9° C.
Temperature of the steam . . . . .	100° C.
First reading of end of pointer . . . . .	5.0 cm.
Second . . . . .	3.3 cm.
Diameter of roller . . . . .	2.0 cm.
Length of pointer . . . . .	19.0 cm.
Distance between marks on tube . . . . .	50.0 cm.

Since the tube is clamped at C, the movement of the mark D represents the total expansion of the length of tube between the two marks ; the expansion of the two overhanging portions obviously does not affect the roller. The movement of the tube causes the roller to turn <sup>2</sup> and with it the pointer. The pointer is 19 cm. long and the roller is 1 cm. in radius ;

<sup>1</sup> The scale should be as close to the pointer as possible, without actually touching. See note on parallax error.

<sup>2</sup> Care must be taken that the pressure of the tube on the roller is sufficient to prevent any chance of the latter slipping back.

hence the end of the pointer moves in the arc of a circle of 20 cm. radius, i.e. 20 times the radius of the roller. Thus the end of the pointer moves 20 times as far as a point on the circumference of the roller.

Now the end of the pointer moved through a distance of 1.7 cm. (It is true that the distance was measured along a straight line, while the end moved in the arc of a circle; for such a small arc, however, we can neglect the error as explained on page 37).

Consequently the point moved through  $\frac{1.7}{20} = .085$  cm.

The rise in temperature was  $(100 - 9) = 91^\circ$ .

Hence the expansion per degree =  $\frac{.085}{91} = .00093$  cm.

Therefore the coefficient of linear expansion

$$= \frac{.00093 \text{ cm.}}{\text{length CD at } 0^\circ \text{ C.}}$$

To obtain the length CD at  $0^\circ \text{ C.}$  we make use of our determination of the expansion per degree. The length of CD was measured at  $9^\circ \text{ C.}$ ; if we cooled the tube to  $0^\circ \text{ C.}$  we see from our results that we should diminish the length by  $9 \times .00093 \text{ cm.} = .0084 \text{ cm.}$  or less than .1 mm. But we measured CD to the nearest mm., and hence should not have been able to detect .1 mm. Hence for this work we can regard 50.0 cm. as sufficiently near the length at  $0^\circ \text{ C.}$  for our purpose.

The coefficient of linear expansion of brass is therefore

$$\frac{.00093 \text{ cm.}}{50.0 \text{ cm.}} = .000019 \text{ (to two significant figures).}$$

**Method II. More Accurate Method Intended to Give Results Trustworthy to about 1 per cent.**—The apparatus was designed to measure the expansion of metal tubes so that the material used in the first method could be used.<sup>1</sup>

The arrangements of the previous experiment are modified in three ways.

<sup>1</sup> For the case of solid rods, see note, page 35.

(1) A more accurate instrument is used for measuring the expansion.

(2) More careful arrangements are made for ensuring that the tube is really at the temperature which it is supposed to be.

(3) Provision is made that the increase in length shall not be obscured by any chance expansion of the measuring apparatus.

The tube is lagged with a thick covering of cotton wool<sup>1</sup> for the whole of its length with the exception of two gaps about 1 cm. long over each of the two marks. Another similar tube also lagged, through which cold water can be passed, is placed parallel to it; this tube is to serve as a constant standard of length. The two tubes are clamped near one end in the special form of clamp illustrated; the two edges B B

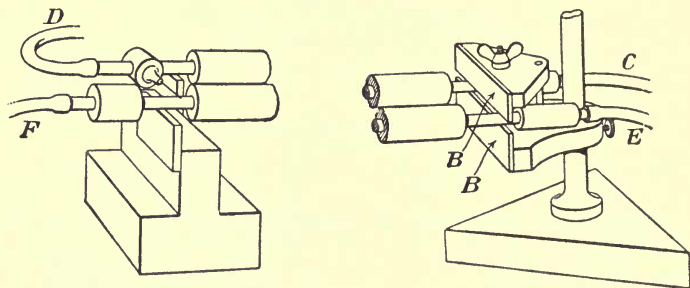


FIG. 17.

(Fig. 17) are of hard wood and are about 3 mm. thick, the remainder of the clamp being iron. The experimental tube is clamped at one of the marks and the portion near the other mark rests in a V-notch in a narrow upright piece of wood screwed to a block. The tube is thus free to expand in this direction. Two fine marks, about 1 mm. apart, are made close to the larger mark and are viewed by means of a microscope fitted with an eyepiece micrometer scale (the ordinary

<sup>1</sup> For convenience in putting on, the cotton wool is wound on a thin cardboard tube which just slips over the brass tube.

mark when viewed through the microscope presents too coarse an outline for accurate measurement and two fine ones are made so that one may be used as a check on the other).

Clamped to the cold water tube is an arm terminating in a fine needle, the point of which is adjusted to be as near as possible to the marks on the experimental tube, so that it is seen through the microscopes at the same time as the marks and serves as a standard of reference.<sup>1</sup> The cold water tube also rests in a notch in a piece of wood placed to one side of the other to allow room for the clamp. Lengths of rubber tubing are connected to each end of the two tubes. Cold water from the tap comes in at C. D is fitted with a piece of glass tubing, which is at first connected to E, so that water circulates through both tubes and passes out at F.<sup>2</sup>

The water is allowed to circulate for some time (e.g. 15 minutes), until the temperature is constant ; this temperature is noted. The position of the pointer and of the fine marks is then read off on the eyepiece scale. E is then uncoupled from D and connected to a boiler so that steam passes through the experimental tube, while cold water continues to pass through the other. The reading of the two marks and the pointer is again noted ; it will be found that the marks move through a considerable distance almost immediately, but do not attain their final position until the steam has been passing for some time, e.g. 10 or 20 minutes. Readings are taken every few minutes until it is quite clear that they have become constant. E is then uncoupled from the boiler and connected to D so that cold water circulates through both tubes ; when everything is steady readings are again taken to see that the tube returns to its original length. As a general rule the reading of the pointer remains the same throughout as the bench does not become heated to any great extent ; sometimes,

<sup>1</sup> It is difficult to get the pointer in focus in the field of view and at the same time not touching the tube ; the writer finds that the most satisfactory arrangement is to use a small electric lamp to illuminate the marks and then one can sight on the shadow of the pointer.

<sup>2</sup> The final outlet should be above the level of the metal tubes to make sure that the latter are always full.



however, there is a shift of  $\cdot 01$  mm. or so, which usually means that all the final readings are different from the initial ones—the bench does not return very quickly to its former condition, or there may have been some slight shift of the microscope—and it is necessary to have the pointer as a check. The pointer also serves as a useful reminder if the observer happens to lean on the bench when taking a reading and so causes a distinct shift. Either before or after the experiment the eyepiece scale is calibrated by focussing the microscope on a millimetre scale and counting the number of divisions which correspond to a whole number of millimetres.

The following figures from an experiment illustrate the method.

Temp. of cold water =  $8^{\circ}$  C. Temp. of steam (bar. = 746 mm.) =  $99\cdot 5^{\circ}$  C.

Readings	1	2	3
Pointer . . .	25·0	25·0	25·0
1st mark . . .	28·2	20·8	28·2
2nd mark . . .	33·8	26·4	33·8

Movement of each mark = 7·4 scale divisions.

Calibration. 3 mm. corresponds to 25·8 scale divisions.

1 scale division =  $\cdot 1163$  mm.

Expansion of the tube =  $7\cdot 4 \times \cdot 116 = \cdot 86$  mm.

Expansion per degree =  $\cdot 86/91\cdot 5 = \cdot 094$  mm.

Coefficient =  $\cdot 094/500 = \cdot 0000188$ .

*Note on the Experiment.*—It will be seen that in order to get the value of the coefficient correct to 1 per cent. the expansion must be measured to an accuracy well within  $\cdot 01$  mm. Travelling microscopes worked by a micrometer screw are made, which read to  $\cdot 01$  or even  $\cdot 001$  mm., but unless they are in good condition and are of first rate design and make, a number of determinations of the distance between two close marks will differ by considerably more than  $\cdot 01$  mm. On the other hand it is not difficult to obtain an eyepiece scale which with a very ordinary microscope will read consistently to  $\cdot 01$  mm. if the focussing is accurate and the illumination good. An eyepiece scale is therefore recommended, and it is also less trouble.

Where the specimen is in the form of a rod and not a tube it must be surrounded by a jacket and project a very small amount from each end (readings taken through a glass jacket are very unreliable unless they are taken through flat windows of optical glass). Supporting the rod by its extreme ends is likely to produce errors due to sagging, and it is better to support it at two points within the jacket (at positions of minimum sagging given by Airey's formula<sup>1</sup>) and use a microscope at each end with a constant temperature standard of length. In this case the arrangement becomes a sort of comparator (page 39); laboratory comparators are made e.g. by the Cambridge and Paul Instrument Company, but they are very expensive, and in few laboratories is a really accurate value for a coefficient required sufficiently often to justify the expense.

#### Note on the Degree of Accuracy of Physical Measurements.

No practical measurement is absolutely exact; it can only be approximate. On the other hand, if the measurement is of use it is most important that the degree of accuracy should be known. Suppose, for example, that the length of a rod is being determined by means of a scale graduated in mm. The scale would be placed so that one end of the rod is as nearly as can be judged opposite to a division, and the observer would then be able to say which division of the scale was nearest to the other end. Thus if the length were recorded as 87 mm. it means that the observer is satisfied that 87 is nearer the length than 88 mm. or 86. In other words, he is satisfied that the length is something less than 87.5 mm. and greater than 86.5 mm.

This might be written  $87 \pm 0.5$  mm., where 0.5 mm. is called the "probable error." With accurate instruments and skilled observers the probable error of any measurement can be made very small, but it cannot be eliminated altogether.

When a result is based on several observations it is easy to be misled as to its accuracy. For example, suppose that the area of a rectangular surface is being calculated. The length and breadth are measured as above to the nearest mm. and

<sup>1</sup> Cp. *Travaux et Memoires du Bureau International des Poids et Mesures*. Vol. II.

found to be, say, 9.4 cm. and 8.6 cm. respectively. At first sight it might be thought that it is legitimate to say

Area of rectangle =  $9.4 \times 8.6 = 80.64$  sq. cm. or for safety's sake 80.6 sq. cm.

But the length is really only known to be between 9.35 and 9.45 cm. and the breadth between 8.55 and 8.65 cm. Now  $9.35 \times 8.55 = 79.9425$  and  $9.45 \times 8.65 = 81.7425$ . Thus we can only say with certainty that the area is between 79.9425 sq. cm. and 81.7425 sq. cm.

Thus the area should be written not as 80.64 sq. cm., but 81 sq. cm. and too much reliance should not be placed on the last figure; the area might be nearer 80 or 82 sq. cm. In fact the result should only be worked out to as many significant figures as the least trustworthy measurement, and even then the last figure is not very reliable.

If the area were recorded as 80.64 sq. cm., not only has time been wasted in useless multiplying, but what is far worse an appearance of accuracy has been given which the measurements do not warrant; it looks as if it might be trusted at least to the first decimal place whereas it is really hardly reliable to the nearest whole number.

It is instructive to examine the results of the experiment described on page 29 from this point of view. The final result depends on three sets of observations, i.e. :—

- (a) The increase in length of a portion of the brass tube.
- (b) The original length of this portion.
- (c) The range of temperature through which the tube is heated.
- (a) In this reading we have to consider the question of the

probable error in reading a mm. scale. The position of a point actually touching the scale might fairly easily be read to the nearest half millimetre, i.e. a good observer could tell whether it was nearer to a division than to a point halfway between the

divisions—a probable error of  $\pm 0.25$  mm. But the pointer must not touch the scale lest it should be slightly bent or the scale moved, and an error due to parallax may be introduced owing to the eye not being exactly opposite to the pointer when taking a reading. Let Fig. 18 represent a plan of the pointer and scale.

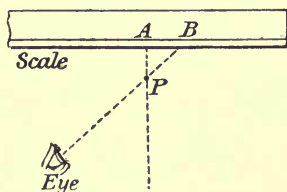


FIG. 18.

The true reading of the pointer is A, i.e. A is directly behind P. But to an eye placed as shown, the reading of the pointer would appear to be at B. The distance AB is the parallax error. The figure of course represents a very exaggerated case, but some error may be introduced. In view of this danger, and also the fact that a very slight want of rigidity in the stands of the clamp and roller might cause a movement of the tube and consequently a greater movement of the pointer we ought not to expect to get a reading for the movement of the pointer with a probable error of less than .5 mm. Hence our reading of 1.7 cm. means anything between 1.65 and 1.75 cm.

The correction for the fact that the end of the pointer moves in the arc of a circle while the distance is measured along a straight line is obtained thus:—

The angle through which the pointer has turned is about  $\tan^{-1} \frac{1.7}{20}$  or a little less than  $5^\circ$ . The difference between the circular measure and the tangent for such an angle is about 1 in 800 (for  $14^\circ$  it is about 1 per cent. and increases rapidly as the angle gets greater).

Hence our correction would be about  $\frac{1.7}{800}$  cm. = .002 cm. As we have already a probable error of .05 cm. we need not trouble about a further .002 cm.

(b) The length of the tube was measured by a mm. scale and found to be 50.0 cm. An error of half a centimetre would only be 1 per cent. of the length; hence our scale is more than sufficiently accurate as a means of measurement, and what is more important, a slight uncertainty as to the exact point held by the clamp does not make this reading less reliable than the others.

(c) Temperature can be determined by means of a fairly good thermometer within about a degree: the temperature of the steam is unlikely to differ from  $100^\circ$  C. by as much as one degree, as this would involve a barometer reading above 787 mm. or below 733. On the other hand, when the steam is passing through the tube, the inside of the latter may take up the temperature of the steam, but the outside is in contact with the air and will be at a lower temperature. In the case of a good conductor like brass the error in estimating the temperature of the tube might be one or two degrees; for a poor conductor it would probably be more.

Thus the range of temperature which we called  $91^\circ$  is not likely to be more, but might easily be two degrees less.

Thus the increase in length per degree might be as high as  $\frac{1.75}{20 \times 89}$  or as low as  $\frac{1.65}{20 \times 91}$ , i.e. anything between  $.000985$  cm. and  $.000905$  cm. Dividing this by 50 cm. the coefficient comes out as between  $.0000181$  and  $.0000197$ . The result given  $.000019$  is therefore barely reliable to the second significant figure; it is, however, more likely to come out too low than too high, so that in any doubtful case the higher value should be taken. It will be seen that the result is likely to be within 5 per cent. of the true value and to this degree of accuracy the method is good enough in the case of metals.

It should be noted also that the result cannot be quite as trustworthy as the least accurate measurement, for even if all the others were absolutely correct, the probable error of this measurement is multiplied by the same factor as the reading itself. Hence it is no use taking elaborate precautions to ensure accuracy for some measurements unless the others are correspondingly precise. It is instructive to consider the second method in the above manner, and trace out how the accuracy of 1 per cent. is justified.

**The Standardization of Measuring Rods.**—The standardization of measuring rods is one of the most important cases where an accurate knowledge of coefficients of expansion is required: it was in connection with this need that the first systematic work was done. Modern methods may be regarded as the development of the work of Roy and Ramsden,<sup>1</sup> influenced also by some aspects of that of Lavoisier and Laplace.

The chief points in Roy's method were: (1) the whole apparatus carrying the measuring instruments was maintained at a constant temperature throughout, being surrounded by melting ice; (2) the increase in length was measured directly by a micrometer combined with an optical arrangement of great accuracy. The chief, if not the only, defect from a mechanical point of view arose from the fact that the measuring instruments were carried on uprights and any want of rigidity in the apparatus would introduce errors. Lavoisier and Laplace<sup>2</sup> had adopted a different

<sup>1</sup> *Phil. Trans.* 1785. The account is well worth reading.

<sup>2</sup> Experiments carried out in 1781 and 1782; the papers published in 1803 contain letters implying the existence of diagrams. J. B. Biot in his *Traité de Physique* (1817) drew figures from the description and



plan: they arranged that the expansion of the rod should be magnified by a system of levers including a tilting telescope, so that in the final experiments an apparent movement of 744 scale divisions corresponded to an expansion of  $\frac{1}{17}$  of a Paris inch. It was difficult to be sure of the exact amount of the magnification and the measurement was less reliable than Roy and Ramsden's direct method.

The chief interest of this method is that in order to obtain rigidity the supports of the lever system were carried on stone blocks (2 feet square by 1 foot thick) on masonry 6 feet deep (the experiments were carried out in the Tuileries gardens); moreover Lavoisier and Laplace pointed out that the most difficult measurement, and that most liable to error, was the temperature determination. They accordingly used thermometers graduated to tenths of a degree, which were compared to a standard.

The modern development of these two pieces of apparatus is the "comparator" designed and used by the International Committee of Weights and Measures at Paris.<sup>1</sup> The comparator is used for comparing the length of any metre scale, heated in succession to different temperatures, with that of a standard metre kept at constant temperature.

Attached to two massive stone pillars are microscopes A A (Fig. 19) as nearly as possible 1 metre apart, and each fitted with a micrometer. The standard metre is placed in one trough, and the scale to be compared with it in another, parallel to the first. The two troughs are carried on a kind of table resting on wheels, which run on three rails, so that first one trough and then the other can be brought under the microscopes. As the table and troughs are very heavy, the rails are carried on a massive bed with a concrete foundation.

The troughs are filled with water, which in the trough containing the standard is kept at a constant temperature, while in the other it is heated to different temperatures in turn. In order to do this the troughs are double walled, the scale being immersed in water in the inner trough, while in the space between the walls circulates water from a reservoir kept at a constant temperature

from his memory. Two sketches were found by the Editor of Lavoisier's works and were published in 1893.

<sup>1</sup> *Travaux et Memoires du Bureau International des Poids et Mesures*. Vol. II.

by means of a thermostat, i.e. an arrangement where the temperature of the water in the reservoir regulates the supply of gas to the burners which are used in heating it. By altering the adjustment of the thermostat any desired temperature can be maintained.

Very efficient stirring apparatus is fitted to the troughs, and the

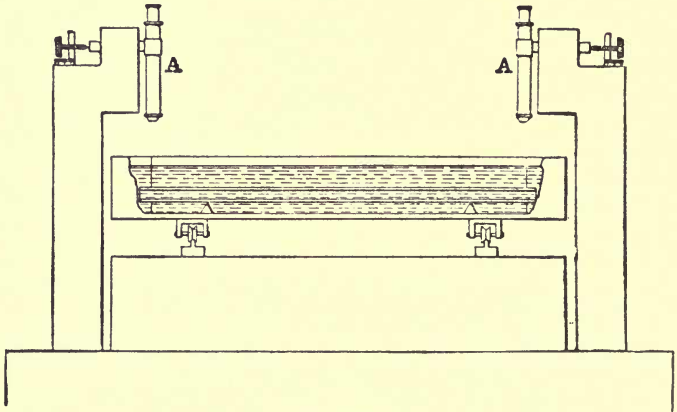


FIG. 19

temperature of the water in the inner trough is given with great accuracy by thermometers which have been carefully studied.

The standard metre is first brought under the microscopes and the micrometers adjusted until their cross wires are over the end marks of the scale; the other trough is then brought under the microscopes and the micrometers again adjusted until the cross wires come over the ends of this scale. The total movement of the two micrometers gives the difference in length between the standard and the other scale. The standard is then again brought under the microscopes, and the micrometers again adjusted. If the readings are not the same as at first it means that there has been some expansion of the supports due to the heating effect of the other trough, and a correction has to be made.

## CHAPTER IV

### PRACTICAL CONSEQUENCES OF EXPANSION

In addition to the case of measuring rods other cases arise where expansion has to be considered. A familiar example is that of railway lines. If the rails were all in one piece their length on a hot day would be considerably greater than on a cold. Take, for example, the line from London to Edinburgh—roughly about 400 miles. Taking the coefficient of linear expansion of iron as  $\cdot 000011$  this length of rail would expand by  $\cdot 000011 \times 400$  miles for each  $1^{\circ}$  C. rise in temperature. A difference of  $25^{\circ}$  C. is quite an ordinary difference between a cold day in winter and a warm day in summer; this represents an expansion of  $25 \times 400 \times \cdot 000011$  miles, or about 194 yards. As the force of expansion is very great, the rails would probably buckle. In consequence a small gap is left between each length of rail and the next to allow for this expansion and contraction.

Below the surface of the earth the variations of temperature between winter and summer are much smaller, and at a depth of a few feet become negligible. At such a depth the temperature is practically constant all the year round. Consequently the rails of tube railways do not require to have gaps between each length, and can in fact be welded together. If, however, the railway comes above ground, gaps have to be left. An example is to be found on the G.N. Piccadilly and Brompton tube; the section between Hammersmith and Baron's Court is above ground and gaps are left between each length of rail, and also between each length of the conductors, from which the motors draw their supply of electricity. As soon as the line gets below ground, these gaps are no longer left. Even

in the case of tramway lines, which are merely embedded a few inches in the ground, it is found that gaps are unnecessary and the rails can be welded together.

Many other examples of expansion are to be found ; water mains exposed to the variations of temperature in air have to be fitted with telescopic joints, and in the same way the tubular girders of the railway bridge across the Menai Straits are mounted on rollers and have a play of several inches. Telegraphic wires can be observed to sag more in hot weather than in cold, and if the wire be put up during hot weather sufficient sag must be allowed for it to have room to contract in cold weather.

**The Behaviour of Glass.**—Glass vessels which are intended for heating, such as flasks, beakers, etc., must have very thin walls ; thick glass would crack. This is because glass is a bad conductor of heat, so that when the outside of the vessel is heated it takes some time for the glass to be warmed throughout. The outside therefore expands, while the inside is still cool and has not expanded, and so the glass is strained and cracks. If the glass is so thin that it quickly gets heated throughout, it can safely be heated as long as the heating is not too sudden or too local.

Since the introduction of the electric furnace it has been possible to make vessels of fused silica, which is not unlike glass in appearance but very brittle and very infusible. Quite thick vessels of this substance can be heated to redness and suddenly plunged into cold water without injury. Silica is a bad conductor like glass, so that there would be great difference in temperature between the inside and outside, but the coefficient of expansion is only about  $\frac{1}{7}$  of that of glass and so the strains are quite small.

Glass of any thickness, which has been heated and allowed to cool quickly, is in a state of great strain due to the unequal contraction. The two scientific toys known as Prince Rupert's drops and Bologna flasks, are well-known examples of this. The former are lumps of glass formed by heating a glass rod and allowing the molten glass to fall in drops into



cold water. The drops form pear-shaped lumps, with a sort of tail, and are in a state of great strain. If the end of the tail be broken off the whole drop flies to pieces with a loud report.

Bologna flasks are simply bulbs blown on the end of a short piece of thick glass tubing and suddenly cooled by plunging the softened glass into an iron mould. If a very small piece of flint be shaken about inside it will make quite small scratches (usually invisible) and cut through the inner layer of glass and disturb the equilibrium. This causes the bottom of the flask suddenly to crack and drop out.

Cheap glass tumblers and dishes sometimes emulate these toys and suddenly crack as the result of a slight knock or the pouring in of hot water. Better quality glass vessels are carefully "annealed" after being made; that is, they are heated almost to the softening point in a muffle, maintained at this temperature for some time so as to get warmed through, and then allowed to cool very gradually. The glass thus contracts evenly and strains are avoided. Such vessels are much less likely to crack. This point must be remembered in all glass blowing work in the laboratory; a sealed joint is almost certain to break if it is allowed to cool quickly.

In many pieces of apparatus it is necessary to have wires passing through the sides of glass vessels, the joint being airtight. To make a successful sealed joint the wire must have the same coefficient of expansion as the glass (since the latter has to be heated to the softening point). Platinum has practically the same coefficient as glass and is therefore the metal largely used (but see p. 49).

Where it is essential to have a wire of different material, much trouble is involved. Thus in making the Coolidge X-ray tube it was necessary to have molybdenum wires at one point. A special glass having a coefficient equal to that of molybdenum was made and the wires passed through a piece of this glass; this glass was then connected to the rest of the tube through a series of intermediate glasses whose



coefficients of expansion differed by such small steps that they could be sealed to one another.

**Applications of the Principle of Expansion.**—The enormous force exerted during expansion and contraction is frequently made use of in the process known as “shrinking.”

For example, in making a cart wheel, the iron tyre is made so that it is a little too small to slip on the wheel. It is made red hot, when it expands, so that it can be slipped over the wheel, which is lying down on the ground. Buckets of water are then poured over it, when it cools and contracts, binding the wheel together, and very firmly secured. An engineer would refer to this as “shrinking” on the tyre, and the process is frequently employed.

For the same reason the rivets used in boilers are put in red hot, so that as they cool they bind the plates closely together. This would not by itself make a sufficiently steam-tight joint for modern high pressures; the edges of the plates are either “caulked” or “fullered” (caulking consists in treating the edges with an instrument like a blunt chisel after they have been rivetted).

When this has been done the fact that the rivets have been put in red hot prevents the plates becoming loose again when the boiler is under steam.

Various types of automatic fire alarms are based on the principle of expansion. A common type makes use of a compound bar of brass and iron, similar to the one described at the beginning of this chapter. It is arranged so that when it becomes hot it bends, and touches the point of a screw, thus completing an electric circuit and ringing a bell. A similar device has been used for indicating whether the rear lamp of a motor car is alight; the compound bar being placed over the lamp, so that as long as the lamp is alight the heat is sufficient to keep the bar bent away from a screw point. If the lamp goes out the bar straightens and touches the screw point and completes an electric circuit and lights a small lamp in front of the driver.

The principle of expansion is applied in the construction of

thermostats. These are arrangements for maintaining a constant temperature. Fig. 20 shows a simple laboratory pattern suitable for a water bath. The thermostat is placed in the bath and the gas supply passes through it to the burner which is doing the heating. The gas comes in by the glass tube D and travels as shown by the arrows to E and so to the burner. The bulb A contains toluene or some similar liquid with a large coefficient of expansion; the lower part of A and the narrow tube contain mercury. When the temperature of the bath rises above a certain value the expansion of the toluene causes the mercury to close B and cut off the gas supply; a small by-pass at C allows sufficient gas to pass to save the burner from being completely extinguished. The adjustment of the precise temperature to be maintained is accomplished by altering the position of the narrow tube B.

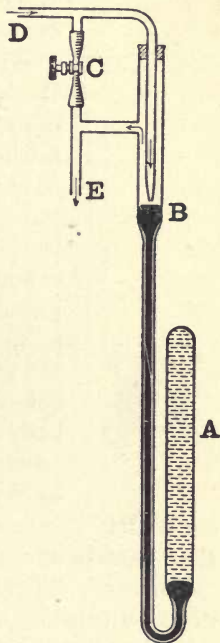


FIG. 20.

**Devices for Compensating the Effect of Expansion.**—The fact that different substances have different coefficients of expansion has been utilized in various compensating devices. The earliest examples are to be found in the case of clocks. The rate of a clock is governed by the time of swing of its pendulum, and this depends on the length (or to be accurate, on the distance between the centre of suspension and a certain point called the centre of oscillation; this last point will not be very far from the centre of gravity of the “bob” if the latter be heavy and the pendulum rod light).

The time of swing of a long pendulum is greater than that of a short one, and consequently when the pendulum of a

clock expands on a warm day the clock would go more slowly ; thus it would tend to lose in warm weather and gain in cold.

Compensating pendulums were designed independently by two clockmakers named Graham and Harrison about 1720, Graham's pendulum being a year or two the earlier.

Fig. 21 shows Graham's pendulum. The rod is of iron, while the bob is formed by two glass tubes containing mercury.



FIG. 21.

When therefore a rise in temperature causes the iron rod to expand, increasing the length of the pendulum, the mercury columns expand, raising the centre of gravity of the bob, and so diminishing the effective length of the pendulum. Mercury expands very much more than iron, so that the expansion of quite a short column of mercury will raise the centre of gravity sufficiently to counteract the expansion of the iron.

The exact amount of mercury to produce compensation was determined by trial for each clock ; the length of the columns has to be about one-sixth that of the rod. It should be noted that the glass tubes increase in diameter, but the expansion of the mercury is much greater than that of the glass.

Harrison's "Gridiron" pendulum is more readily understood by considering a modern variation. In Fig. 22 A is a crosspiece firmly attached to two steel rods I, I. These carry at their lower ends crosspieces B, to which are attached zinc rods Z, Z. These are connected at the top by a crosspiece to which is attached a steel rod S, carrying the bob of the pendulum.

The expansion of the steel rods carries the bob downwards through a distance equal to the expansion of S plus the expansion of one of the rods I (since S itself is supported by I, I and would be carried down through a distance equal to the expansion of either). The expansion of the zinc rods

carries the bob up through a distance equal to the expansion of either rod.

Now since the coefficient of expansion of zinc is about two and a half times that of steel, it follows that by making the length of I and S about two and a half times that of Z the expan-

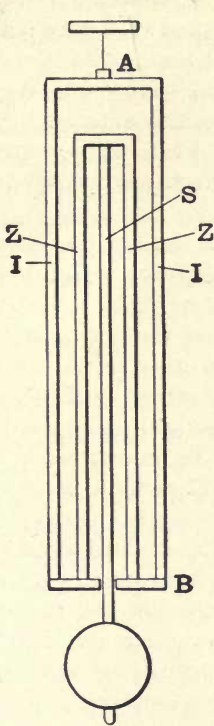


FIG. 22.

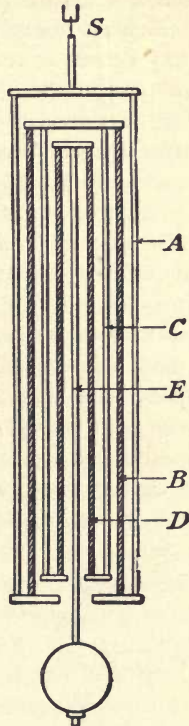


FIG. 23.

sion will just balance and the effective length remain constant.

In the original pendulum Harrison used brass and steel, and since the coefficient of the expansion of brass is only about one and a half times that of steel the combined length of the steel bars must be one and a half times that of the brass. Since this clearly could not be done with the two pairs of rods

used in the more modern form, he used five rods of steel and four of brass as shown in Fig. 23.

It will be clear that the total length of A, C, E and the small piece from S to the crosspiece must be one and a half times the total length of B and D. Harrison made a great many experiments before he obtained a satisfactory result, since the coefficients of expansion of brass and steel were not known with any degree of accuracy at that time (1725).

In actual practice the pendulums have to be over compensated, because the rate of a clock is affected by change of temperature in other ways than by alteration in the length of the pendulum, and these other effects are corrected by this over compensation.

In the case of chronometers and watches the rate is controlled by the oscillation of the balance wheel under the influence of a spring (the "hair spring"). The time of oscillation depends on the stiffness of the spring and on the mass and shape of the wheel. An increase in diameter of the wheel (the mass remaining the same) would cause it to oscillate more slowly (just as a flywheel of larger diameter is more difficult to start or stop), while an increase in stiffness in the spring would make the wheel oscillate more quickly.

A rise in temperature would increase the diameter of the wheel, and diminish the stiffness of the spring, both of these tending to increase the time of oscillation and so make the watch lose. To counteract this the rim is made in two (sometimes three or four) sections, each section being fixed to a spoke. The sections are compound bars of iron and brass, with the brass on the outside, and carry weights on their

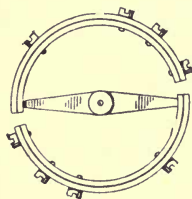


FIG. 24.

tremities (see Fig. 24).

A rise in temperature causes these sections to curl inwards, carrying the weights with them, so diminishing the effective diameter and compensating for the expansion of the spokes and the diminished stiffness of the spring. This device is



due originally to Harrison, although various improvements have been made since his time.

**Compensated Measuring Rods.**—It will be obvious that a measuring rod might be constructed on the same principle as Harrison's pendulum. It would, however, be somewhat inconvenient and unnecessarily complicated. A simpler form was designed by General Colby for the Indian Survey and has been used since.

In the construction of machinery the different parts are likely to be made at different times and under different conditions. Since the dimensions of the parts often have to be accurate to  $\frac{1}{10000}$  inch, or in some cases  $\frac{1}{100000}$  inch, or even less, it is clear that a part made to size on a warm day would not fit in with a part made on a cold one. To get over this difficulty the gauges used in testing the parts should be made of the same metal as the parts themselves; the expansion of the gauge will then just balance the expansion of the part, and when they are assembled they will fit, in spite of being made at different temperatures.

**The Properties of Nickel Steel.**—In the course of an extended research on the properties of nickel steel, M. Guillaume discovered that the coefficient of expansion is very much influenced by the percentage of nickel. Two particular alloys are of importance, that containing 36 per cent. of nickel and that containing 45 per cent. of nickel.

The former has a much smaller coefficient of expansion than alloys containing a greater or less proportion of nickel; to this alloy M. Guillaume gave the name of *Invar*. The coefficient of linear expansion of a specimen of invar depends on the conditions under which the alloy is formed. It ranges from about  $\cdot 00000025$  down to zero and may even be negative. It appears to be impossible to arrange the conditions beforehand so that the product shall have a particular coefficient of expansion; but all pieces from the same ingot have the same coefficient and it is only necessary to test one specimen from each ingot when made.

The 45 per cent. alloy has a coefficient equal to that of

platinum, and consequently can be sealed through glass. In view of the increasing difficulty of obtaining platinum this is most important.

Many of the compensating devices already considered have been rendered obsolete by the discovery of invar. An invar tape stretched under a constant known tension is much used in survey work ; the tape hangs in a curve of definite shape and the distance between two marks near the points of support is determined beforehand on a comparator.

Another important use is in clock pendulums. Even in the case of the variety of invar with the largest coefficient of expansion, the ratio of the coefficient of invar to that of iron is about the same as that of iron to mercury, and consequently a pendulum can be made on Graham's principle with an invar rod and an iron bob.

The bob is made in the form of a cylinder, bored so that it slips over the invar rod, and rests on a nut screwed on the lower end of the rod. By making the cylinder of the right length, exact compensation can be obtained, and this construction is now very largely used. It is more satisfactory than using a variety of invar with a zero coefficient for pendulum construction, as the pendulum can be over compensated for expansion so as to balance the other slight errors of the clock, to which reference has already been made.

M. Guillaume points out that other alloys of nickel steel may be used with advantage for gauges and scales in engineering workshops, since by altering the percentage of nickel an alloy can be made having a coefficient of expansion equal to that of any varieties of steel with which the workshop may deal.

## CHAPTER V

### EXPANSION OF LIQUIDS

In the last two chapters we have been considering the linear expansion of solids ; that is to say, we were concerned only with changes of length. When a solid is heated, however, changes take place in breadth and thickness as well as in length. Thus if we have a sheet of metal and heat it, the length and breadth increase and consequently the area of the sheet increases. This increase is spoken of as "superficial expansion," and the coefficient of superficial expansion is defined as "the fraction of its original area by which the area of the sheet increases for each degree rise in temperature," or in other words, the coefficient is equal to.

$\frac{\text{increase in area per degree}}{\text{original area}}$ , the original area being regarded as the area at 0° C.

Since the length, breadth and thickness of a solid change on heating, the volume must change. This is referred to as cubical or volume expansion, and the coefficient of cubical expansion is defined as in the other cases as the fraction of its original volume by which a substance expands for each degree rise in temperature.

Thus in general we may say that coefficient of (linear, superficial, cubical) expansion

$$= \frac{\text{increase in (length, area, volume) per degree}}{\text{original (length, area, volume)}}$$

**The Relation Between the Three Coefficients of Expansion of a Solid.**—Consider a solid sheet of length  $a$  and breadth  $b$  (measured at 0° C.). Let the coefficient of linear expansion of the material be  $f$ . Let the temperature of the

sheet be raised from  $0^{\circ}\text{C.}$  to  $1^{\circ}\text{C.}$  Then increase in length of the sheet is  $f \times \text{original length} = fa$ .

Hence the new length of the sheet is  $a + fa = a(1 + f)$ .

Similarly the breadth increases by  $fb$  and the new breadth is  $b + fb = b(1 + f)$ .

Hence the new area  $= a(1 + f) \times b(1 + f)$   
 $= ab(1 + f)^2$

Now the original area was  $ab$ .

Hence increase in area  $= ab(1 + f)^2 - ab$ .

Now coefficient of superficial expansion

$$\begin{aligned} &= \frac{\text{increase in area per degree}}{\text{original area}} \\ &= \frac{ab(1 + f)^2 - ab}{ab} \\ &= (1 + f)^2 - 1 \\ &= 2f + f^2. \end{aligned}$$

Now  $f$ , the coefficient of linear expansion, is always a small quantity; consequently  $f^2$  is very small indeed, and for all ordinary purposes can be neglected in comparison with  $f$ . An example will make this clear. Suppose  $f$  were equal to  $\cdot 00002$ , which, as we have seen, is a fairly high value. Then  $f^2$  would be  $\cdot 000,000,0004$ . From what has been said in Chapter III it will be readily understood that we are not likely to have a value for  $f$  so accurate that we need trouble about corrections in the sixth significant figure. *Hence we may say that the coefficient of superficial expansion is twice the coefficient of linear expansion.*

Again, suppose we have a rectangular block of length  $a$ , breadth  $b$ , depth  $c$ , measured at  $0^{\circ}\text{C.}$  The volume of the block is then  $a \times b \times c$ . Now let the temperature be raised through  $1^{\circ}$ , the coefficient of linear expansion of the material being  $f$  as before.

Then, as we have just seen, the length becomes  $a(1 + f)$ , the breadth  $b(1 + f)$ , and similarly the depth becomes  $c(1 + f)$ .

Thus the volume of the block becomes

$$a(1 + f) \times b(1 + f) \times c(1 + f) = abc(1 + f)^3$$

Thus the increase in volume =  $abc(1+f)^3 - abc$ .

And coefficient of cubical expansion

$$\begin{aligned} &= \frac{\text{increase in volume per degree}}{\text{original volume}} \\ &= \frac{abc(1+f)^3 - abc}{abc} \\ &= (1+f)^3 - 1 \\ &= 3f + 3f^2 + f^3. \end{aligned}$$

Now we have seen that  $f^2$  can be neglected in comparison with  $f$ ; much more then can  $f^3$  be. We can therefore neglect  $3f^2 + f^3$  and say that *the coefficient of cubical expansion is three times the coefficient of linear expansion.*

### EXPANSION OF LIQUIDS.

A liquid has no definite shape of its own, but takes up that of the vessel containing it; we can therefore only be concerned with volume changes.

If we place some liquid in a vessel, as in Chapter I (Fig. 2), and heat it, the vessel expands as well as the liquid, and what we actually observe is the excess of the expansion of the liquid over that of the envelope. If we measure this expansion and neglect the expansion of the vessel we are said to be determining the apparent expansion of the liquid, and we speak of the coefficient of apparent expansion. To obtain the coefficient of absolute or real expansion we should have to know the expansion of the vessel, or else we should adopt the method explained later on page 62.

In speaking of the coefficient of apparent expansion, it is usual to assume that the containing vessel is made of glass unless the contrary is stated.

#### Methods of Determining the Coefficient of Apparent Expansion of a Liquid.

I. *The Volume Dilatometer.*—This instrument consists of a graduated tube of small bore, open at one end and terminating at the other in a bulb, so that it is like a large thermometer.



The liquid is placed in the apparatus so as to fill the bulb and the lower part of the stem,<sup>1</sup> and the whole is placed in melting ice so that the surface of the liquid is just visible above the ice. The position of the surface of the liquid is noted as soon as it remains steady. The apparatus is then placed in a water bath maintained at some definite temperature, e.g. 50° C., care being taken that the liquid is only just visible above the water surface. The position of the liquid in the stem is again noted.

If the area of cross section of the tube is known, the increase in volume is at once obtained by multiplying the distance between the two positions of the surface by this area. Dividing this increase by the temperature range (in our case 50°) gives the mean increase in volume per degree. To obtain the coefficient of apparent expansion we must divide by the original volume of the liquid. In order to use the instrument we must therefore know the volume of the bulb and the area of cross section of the tube, or what comes to the same thing, the volume of the tube between each graduation.

The most accurate way of finding these volumes is to find the weights of some liquid of known density (preferably mercury, which does not wet the surface), which fill the bulb and a known length of the stem respectively. This can be done once for all and the instrument thereby calibrated; it is, however, more usual to adopt some form of weight dilatometer in which the liquid itself is used in the manner described below.

II. *Laboratory Method using a Specific Gravity Flask.*—A specific gravity flask is weighed; it is then filled with the liquid at the temperature of the room (which should be noted). The stopper is replaced and the excess of liquid which has overflowed from the small hole carefully wiped off from the outside. The flask is weighed again. It is then placed in a beaker of water maintained at some temperature, e.g. 60° C. It should be immersed to such a depth that the neck

<sup>1</sup> The filling is accomplished in the same way as in the case of a thermometer.

is just above the surface of the water, but the lower end of the stopper is below (Fig. 25). If the liquid is lighter than water the flask may have to be fastened in some way.

The expansion of the liquid causes some of it to come out through the opening and this should be wiped off. When no more comes out the flask is removed and allowed to cool; the outside is dried and the flask and its contents weighed.

It will be convenient to take some actual results in order to illustrate the way in which the coefficient is worked out.

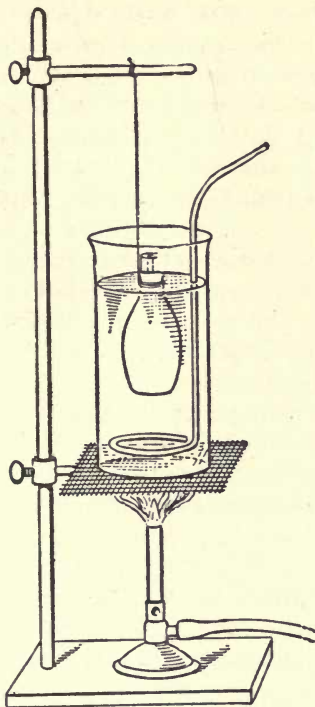


FIG. 25.

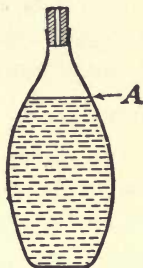


FIG. 26.

Weight of flask empty . . . . .	15.45 gms
Weight of flask full of turpentine at 15° C. . . . .	68.30 gms
Weight of flask and turps after heating to 60° C. . . . .	66.11 gms

Consider the liquid left in the flask. Before heating, this liquid was not able to fill the flask, but would have filled up to the level A (Fig. 26). The remaining space was filled up by  $68.30 - 66.11$  gms. = 2.19 gms., the weight of the liquid which has come out.

At 60° C., however, the liquid left in is sufficient to fill the

flask. (Since we are dealing with apparent expansion we regard the volume of the flask as constant; actually, of course, it is larger at  $60^{\circ}\text{C.}$  than at  $15^{\circ}\text{C.}$ )

Let  $a$  represent the volume of the bottle up to  $A$  and  $b$  represent the volume of the rest of the bottle. Then  $a$  c.c. of liquid at  $15^{\circ}\text{C.}$  expand  $b$  c.c. when heated from  $15^{\circ}$  to  $60^{\circ}\text{C.}$  Notice that it is the *volume of liquid left in the flask* which expands  $b$  c.c. The whole flask full of liquid expands by the amount represented by the volume of expelled liquid measured at  $60^{\circ}\text{C.}$ , which is bigger than  $b$ , the volume of the expelled liquid at  $15^{\circ}\text{C.}$

To determine  $a$  and  $b$  we have that  $a$  c.c. of turpentine at  $15^{\circ}\text{C.}$  weigh  $66.11 - 15.45 = 50.66$  gms., and  $b$  c.c. of turpentine at  $15^{\circ}\text{C.}$  weigh  $2.19$  gms. But since we are dealing with the same liquid at the same temperature the volumes are proportional to the weights, i.e.  $a : b$  as  $50.66 : 2.19$ .

Thus we may say that  $50.66$  volumes of turpentine at  $15^{\circ}\text{C.}$  expand  $2.19$  volumes for a rise in the temperature of  $45^{\circ}$  (a "volume" represents the volume of  $1$  gm. of turpentine at room temperature). Thus the expansion per degree is  $\frac{2.19}{45}$  volume.

To get the coefficient we must divide this by the original volume at  $0^{\circ}\text{C.}$  Now the original volume at  $15^{\circ}\text{C.}$  was  $50.66$  "volumes," and since the expansion per degree is  $\frac{2.19}{45}$  volumes, the expansion for  $15^{\circ}\text{C.}$  is  $\frac{2.19}{45} \times 15 = .73$  volumes. Thus the volume at  $0^{\circ}\text{C.}$  would have been  $50.66 - .73 = 49.93$  volumes. Thus coefficient of apparent expansion

$$= \frac{2.19}{45 \times 49.93} = .00097.$$

Notice that in dealing with liquids such as turpentine, with a fairly high coefficient of expansion, we can no longer consider the original volume at  $15^{\circ}\text{C.}$  as being a sufficiently near approximation; we must either start the experiment at  $0^{\circ}\text{C.}$  or else deduce the volume at  $0^{\circ}\text{C.}$  from our readings. The latter course is preferable in the experiment described,

for if we filled the flask at  $0^{\circ}$  C. and then attempted to weigh it at the room temperature the liquid would be oozing out while the weighing went on.

The principle of the above method is sound, but a specific gravity flask is not suitable for accurate work as the overflow of the liquid is uncertain ; some other form of apparatus must be used. A form which works well with mercury is the weight thermometer (Fig. 27). It is filled with mercury in the manner described in Chapter II, i.e. some air is expelled by heating and the open end of the tube dipped under clean mercury in a dish ; some mercury enters as the bulb cools. The mercury in the bulb is then boiled for some time to remove gases condensed on the inner surface of the glass, and then allowed to cool with the end of the tube dipping under mercury.

The experiment is performed in much the same way as in the case of the specific gravity flask. The bulb is first surrounded with melting ice, the end of the tube still dipping under mercury. The apparatus is thus full of mercury at  $0^{\circ}$  C. It is then taken out and weighed, any mercury which escapes owing to expansion as its temperature rises to that of the room being caught in a small crucible and weighed with the rest. The apparatus is then placed in a bath at any convenient temperature and the expelled mercury caught in a small dish and weighed. The loss in weight of the apparatus may also be determined as a check. The calculation of the coefficient is performed as before, except that the "volume" at  $0^{\circ}$  C. is determined directly instead of having to be calculated.

The weight thermometer is not suitable for general use, as

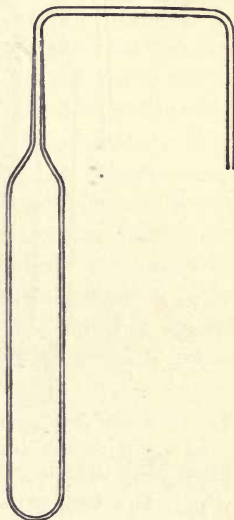


FIG. 27.

it is tedious to fill and almost impossible to clean out. A more useful form is shown in Fig. 28; the tubes are of fine bore and a mark is made at A. The apparatus is filled and by judicious tilting the liquid is made to flow out of B until the surface in the other tube is at A. This procedure is repeated

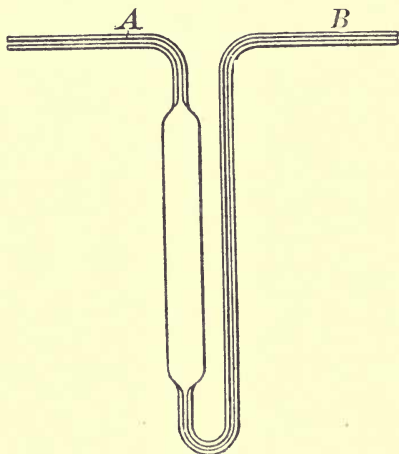


FIG. 28.

at the high temperature before taking out the apparatus and weighing. In any accurate work, water baths maintained at a constant temperature by a thermostat must be employed and the instrument kept in the bath for a long time. Such instruments are known as pycnometers.

Although the weight thermometer is not suitable for general use in determining coefficients it is useful as means of measuring temperatures (hence its name). It is

filled with mercury at  $0^{\circ}$  C. and then placed in the liquid of which the temperature is to be found, and the weight of mercury expelled is determined. The weight expelled when the instrument is heated to  $100^{\circ}$  C. is also found and from these weights the temperature is found. The method, although troublesome, has advantages in that no calibration of the tube is required, and uncertainties as to the zero are avoided as the first weighing is at  $0^{\circ}$  C.

**Absolute or Real Expansion.**—The pycnometer gives us a means of determining apparent expansion. If we knew the expansion of the vessel we could then apply a correction and deduce the absolute expansion of the liquid. Now the absolute expansion of mercury has been determined by the method, explained at the end of the chapter, and is known



with great accuracy. We can therefore standardize any pycnometer once for all by determining the coefficient of apparent expansion of mercury in it; the difference between this and the coefficient of absolute expansion gives the correction due to the expansion of the vessel. Mercury is very suitable for this purpose, as in addition to its other advantages its coefficient of expansion is small as compared to such liquids as alcohol or turpentine; the expansion of the vessel therefore makes a considerable difference between the real and apparent expansion of mercury. It may be noted that for volatile liquids of low density some form of volume dilatometer standardized by mercury is better than a pycnometer.

**Use of Fused Silica Vessels.**—We have already seen that fused silica has a very small coefficient of expansion, about the same order as that of invar. The volume expansion of silica is only about 1 per cent. of that of mercury and much less than 1 per cent. of that of many liquids. Consequently for all work except that of the very highest accuracy, a determination of the coefficient of expansion of a liquid in a silica pycnometer or volume dilatometer may be regarded as giving the coefficient of absolute expansion.

**The Expansion of Water.**—In the case of most liquids the coefficient of expansion over a moderate range of temperature is approximately constant: that is to say the increase of volume from say  $10^{\circ}$  C. to  $20^{\circ}$  C. (as measured by a mercury thermometer) is about the same as that from  $20^{\circ}$  C. to  $30^{\circ}$  C. or  $30^{\circ}$  C. to  $40^{\circ}$  C. In the case of water, however, this is not even approximately true, the coefficient at high temperatures being much greater than at low. Moreover, if some water at  $0^{\circ}$  C. is gradually heated it contracts until its temperature is about  $4^{\circ}$  C. and then expands as the temperature rises, so that its volume at  $8^{\circ}$  C. is very nearly the same as at  $0^{\circ}$  C.: the expansion then continues at an increasing rate as the temperature rises.

This effect may be investigated by using a volume dilatometer with a very fine stem; but as the volume changes in the neighbourhood of  $4^{\circ}$  C. are very small, it will be necessary

to use a fused silica vessel to show them directly. With a glass vessel standardized by mercury the changes can be deduced from the observations. The following experiment is an example of a simple and fairly quick way of obtaining some idea of the magnitude of the effect.

A fused silica pyknometer was filled with water. It was slightly tilted, so that the water in the tube B (which is of

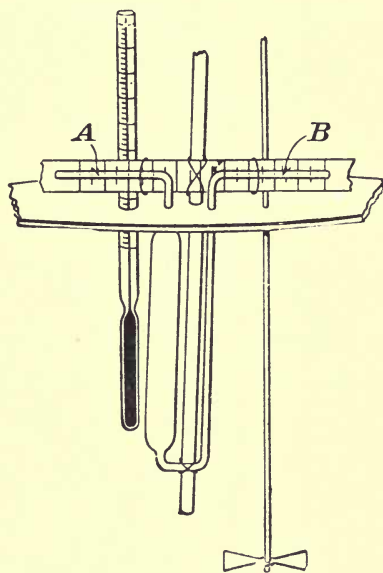


FIG. 29.

smaller bore than the other) ran to the open end (Fig. 29). The effect of surface tension is to prevent the water coming out unless there is sufficient pressure, and the tilt was not enough to do this but only to ensure the surface being at the end of B. A small mark was made near the surface of the water in A. The pyknometer was placed in a large beaker of water (about 2 litres) provided with a very efficient mechanical stirrer. This latter is essential. The pykno-

meter was wired to an upright glass rod held in a clamp; a good thermometer reading to  $\frac{1}{10}$  degree being fastened with its bulb near to it. Fastening was needed to avoid the instruments being washed about by the circulating water.

The distance of the surface in A from the mark was read with a glass mm. scale. Small pieces of ice were added until the thermometer read about  $8^{\circ}\text{C}$ .; the temperature was maintained at this for about five minutes and the distance of the surface A from the mark measured. More ice was

added until the temperature fell to 6° C. and the process repeated.

Readings were taken at 4° C., 2° C., and as near 0° C. as it was possible to get in a reasonable time. Some of the cold water was then syphoned out and enough tap water added to bring the temperature up to 2° C. again. In this manner readings at 4°, 6°, 8°, and 10° C. were obtained. The whole experiment took about an hour. The readings were taken to 0.5 mm., and the figures obtained were as follows:—

Temperature.	Distance of Surface from Mark.	Temperature.	Distance of Surface from Mark.
10.7° C.	+ 1.5 mm.	2°	- 2.0 mm.
8°	- 1.0 mm.	4°	- 2.5 mm.
6°	- 2.0 mm.	6°	- 2.0 mm.
4°	- 2.5 mm.	8°	- 1.0 mm.
0.7°	- 1.5 mm.	10.9°	+ 1.0 mm.

Fig. 30 shows the results graphically.

The diameter of the tube A was found by a micrometer microscope to be about .9 mm., each mm. length therefore represents a volume of  $.1 \times \pi \times (.045)^2 = .00064$  c.c. about. It so happened that the volume of the dilatometer was about 6.4 c.c., so that each mm. on the tube represented about .0001 of the volume of water.

It will be seen that the graph is nearly symmetrical about 4° C.; 1 c.c. of water at 4° C. expands about .00005 c.c. if heated to 6° C. or cooled to 2° C., and about .00015 c.c. if heated to 8° C. or cooled to 0° C.<sup>1</sup>

It may be noted that since the coefficient of cubical expansion of glass is about .000025 the apparent expansion of water in a glass vessel would not begin until somewhere about 6° C.

At about 4° C. a given mass of water occupies the smallest

<sup>1</sup> More accurate work gives values about .000038 and .00012 respectively.

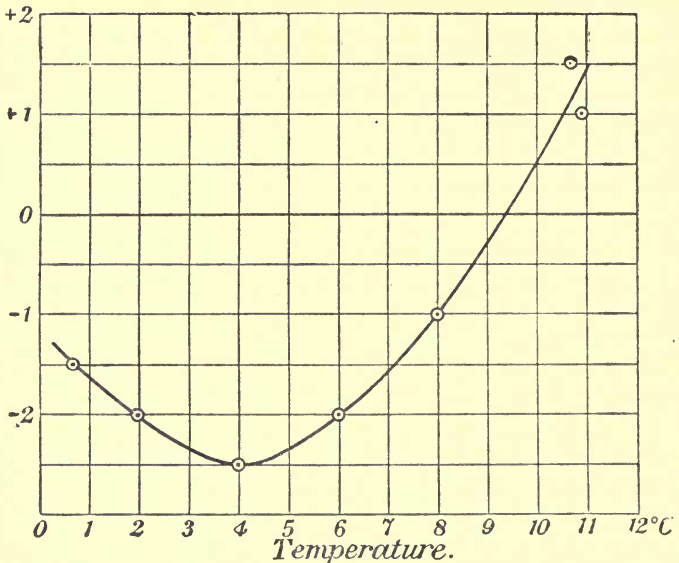


FIG. 30.

possible volume; this temperature is therefore taken in defining the gramme. Much work has been done in finding the exact temperature of maximum density; the most accurate is probably that of Joule and Playfair.<sup>1</sup> The mean of their experiments gave the temperature as  $3.95^{\circ}\text{C}$ .

#### The Determination of the Absolute Expansion of Mercury.—

The first experiments on the expansion of mercury in which the expansion of the vessel is not involved<sup>2</sup> were performed by Dulong and Petit about 1816, and their method was improved by Regnault in 1842. Their method consisted in comparing the densities of mercury at different temperatures. If the density of a liquid at two different temperatures is known the expansion between those temperatures can be at once worked out. For suppose we knew that the density of a certain liquid at  $0^{\circ}\text{C}$ . was  $\cdot 667$  gms. per c.c. and at  $100^{\circ}\text{C}$ . was  $\cdot 65$  gms. per c.c., we could proceed as follows:—

<sup>1</sup> Joule's *Scientific Papers*. Vol. II.

<sup>2</sup> See note at the end of the chapter on the expansion of glass vessel.

If we weigh out say 50 gms. of the liquid, we shall have 50 gms. of it whatever the temperature; the mass will not alter. The volume will however vary. Thus at 0° C. the liquid would

occupy  $\frac{50}{.667} = 75$  c.c. : at 100° C. it would occupy  $\frac{50}{.65} = 77$  c.c.

Thus our liquid would occupy 75 c.c. at 0° C. and 77 c.c. at 100° C. ; we know then that 75 c.c. at 0° C. becomes 77 c.c. at 100° C., and with a different mass of liquid the volumes would be proportional. We do not even require to know the densities separately, but only their ratio, since for any given mass X

$$\frac{\text{volume at } 0^{\circ} \text{ C.}}{\text{volume at } 100^{\circ} \text{ C.}} = \frac{\frac{X}{\text{density at } 0^{\circ} \text{ C.}}}{\frac{X}{\text{density at } 100^{\circ} \text{ C.}}} = \frac{\text{density at } 100^{\circ} \text{ C.}}{\text{density at } 0^{\circ} \text{ C.}}$$

The problem, therefore, resolves itself into finding some means of comparing the density of a liquid at different temperatures.

Dulong and Petit adopted the U tube method. The principle of this method (which may be found in any elementary textbook of hydrostatics) may be briefly illustrated as follows.

Let Fig. 31 represent two vertical tubes of different diameter connected by a horizontal tube. If any liquid is put in it will stand at the same level in each tube (neglecting the effect of surface tension, see page 66). The two upright columns of liquid therefore balance. They are not of the same weight (for the tubes are of different size) but the hydrostatic pressure, i.e. pressure per unit area at the base of each column, is the same, otherwise the force across a section A from left to right would not be equal to the force from right to left and movement would take place.

If the liquid in the two upright tubes were of different densities, the two columns would balance when they produced equal hydrostatic pressure at their bases. Let the height of the right-hand column be  $h$  and that of the left-hand column  $h'$ . The pressure per unit area due to a column of height  $h$  is simply the weight of a column of liquid of unit cross section and height  $h$ , and does not depend on the size or shape of the tube (cp. the well-known "hydrostatic paradox" of Pascal). Hence if the two columns balance we know that although their weights may be different the weight of a column of the right hand liquid of unit cross-



section and height  $h$  is equal to the weight of a column of the left hand liquid of unit cross-section and height  $h'$ .

These weights are obviously  $h \times$  weight of unit volume of right-hand liquid and  $h' \times$  weight of unit volume of left-hand liquid.

Thus  $\frac{h}{h'} = \frac{\text{weight of unit volume of left hand liquid}}{\text{weight of unit volume of right hand liquid}} = \frac{\rho'}{\rho}$

where  $\rho$  and  $\rho'$  are the densities, since the weights of unit volumes

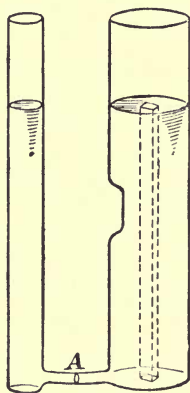


FIG. 31.

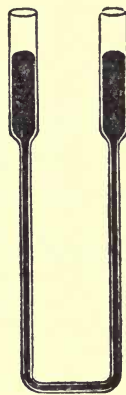


FIG. 32.

are proportional to the densities. Thus whatever the size and shape of the tubes, we know that when the two columns balance

$\frac{h}{h'} = \frac{\rho'}{\rho}$ . Dulong and Petit used a U tube of the shape shown in

Fig. 32; the upright tubes were 55 cm. long, and the horizontal tube was of narrow bore. One vertical tube was surrounded by an iron jacket containing pieces of ice and the other by a copper jacket containing oil which could be heated by a furnace built round the jacket. The amount of mercury was such that it could just be seen above the cover of the oil jacket, while the surface in the cold limb could be viewed through a small opening in the iron jacket.

The temperature of the oil was given by an air thermometer and also by a mercury weight thermometer; <sup>1</sup> the bulbs of these

<sup>1</sup> It might appear absurd to measure the expansion of mercury over a rise of temperature which was itself determined by a mercury ther-

were made almost as long as the limb of the U tube, so as to give as nearly as possible the mean temperature of the oil.

As soon as a steady state was reached, the difference between the levels of the mercury surfaces was determined by a cathetometer reading to  $\frac{1}{10}$  mm. The height of the cold column was also determined. Experiments were performed with the oil at various temperatures, the highest being 350° C. At the higher temperatures the indication of the mercury weight thermometer differed from that of the air instrument; the latter was taken to be correct in these cases. In this way the density of mercury at various temperatures was compared to its density at 0° C.

The coefficient of expansion was then deduced as already explained on page 63. An example will make this clear. Suppose that with the oil at 100° C. the difference in the heights of the columns was .925 cm. and the height of the cold column was 50.65 cm. Since the mercury had settled to a steady state before this measurement was made it follows that the hot and cold columns balance. So that whatever the size of the tubes

$$\frac{\text{density of the hot mercury}}{\text{density of the cold mercury}} = \frac{50.65}{51.575}$$

This is all the experiment tells us.

But consider any given mass X gms. of mercury.

If the X gms. occupy  $V_0$  c.c. at 0° C. and  $V_{100}$  c.c. at 100° C. we have already seen that

$$\frac{V_0}{V_{100}} = \frac{\rho_{100}}{\rho_0} = \frac{50.65}{51.575}$$

Since we are dealing with a constant mass X gms. we can say  $V_0$  c.c. at 0° become  $V_{100}$  c.c. at 100°, so that the coefficient

$$\text{of expansion is } \frac{\text{expansion per degree}}{\text{original volume}} = \frac{V_{100} - V_0}{V_0 \times 100} =$$

$$\frac{1}{100} \left( \frac{V_{100} - V_0}{V_0} \right) = \frac{1}{100} \left( \frac{V_{100}}{V_0} - 1 \right) = \frac{1}{100} \left( \frac{51.575}{50.65} - 1 \right).$$

$$\text{That is } \frac{1}{100} \left( \frac{51.575 - 50.65}{50.65} \right) = \frac{1}{100} \cdot \frac{.925}{50.65} = .000183.$$

This is the coefficient of real expansion, since the measurements were performed after the tube had done expanding and under

mometer. Dulong and Petit expressly state that the object of this part was to detect irregularities produced by the expansion of the glass of the weight thermometer.

conditions where the size of the tube does not affect the ratio of the heights.

**Regnault's Improvement of Dulong and Petit's Method.**—Regnault (1842) designed an apparatus to avoid certain defects of the older method. These defects are: (1) the surface of the hot column of mercury had to project above the cover of the oil bath in order to be visible, and consequently the upper part of the column was cooler than the rest; (2) the arrangement involved an error due to surface tension. The effect of surface tension is to make a liquid behave as if its surface formed an elastic membrane (although no such membrane exists).

The surface of mercury in a tube being convex, the effect of surface tension will be to increase the pressure at the bottom of the column and this effect will be considerable if the tube is narrow.

Now surface tension diminishes very rapidly as a liquid is heated, and consequently the effect due to the surface of the hot column of mercury will not balance that due to the surface of the cold, and an error will be introduced. This is diminished by making the tubes as wide as possible, which Dulong and Petit did. If, however, the tube is very wide, the glass must be fairly thick, which does not conduce to accuracy in reading, and the weight of the mercury becomes unmanageable unless the length of the limbs is small. Regnault therefore designed an apparatus in which the two mercury surfaces observed were at the same temperature.

His apparatus is shown diagrammatically in Fig. 33.

The upright limbs AB and CD were of iron, about 150 cm. long and 1 cm. internal diameter. The connecting tube AC was about 3 mm. diameter, as were BF and DE. The tubes GF and LE were of glass and were connected together, and to a pipe which led to a reservoir of compressed air. The cross tube AC had a small hole at K so that the mercury in AC was exposed to atmospheric pressure. The limb AB was surrounded by an oil bath provided with a stirring apparatus and a constant volume air thermometer P, the bulb of which extended the whole length of AB. CD was surrounded by a jacket through which cold water was run and cold water was made to trickle over the horizontal tubes. The pressure of the air in the reservoir was adjusted so that the mercury in GF was nearly at the bottom of the tube,

there being sufficient mercury in the whole apparatus to ensure that the tube AC was full up to the hole K. The tube AC was made accurately horizontal and the heights  $H$ ,  $H'$ ,  $h$  and  $h'$  measured by cathetometers.

Let  $T$  be the temperature of the cold mercury and  $T'$  that of the hot. Let us further suppose that the temperature of the

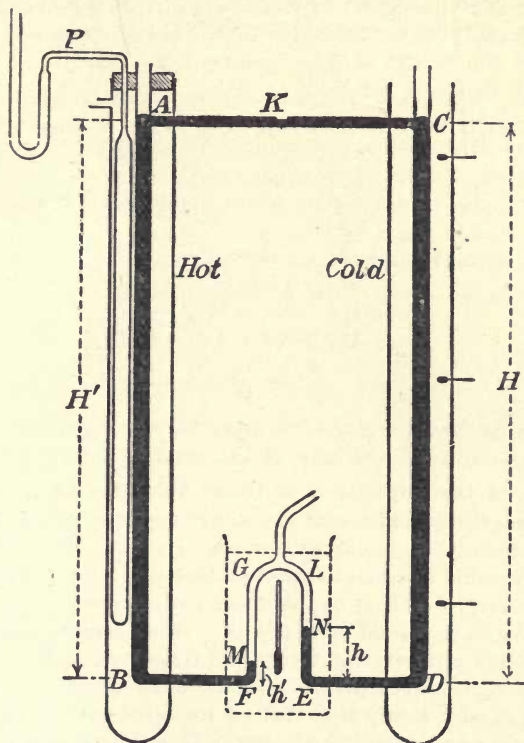


FIG. 33.

mercury in the two limbs  $G$  and  $L$  is also  $T$ ; if it is not a correction will have to be applied, but it will be small since the temperature (which is indicated by the thermometer  $L$ ) will not differ much from  $T$ .

Since the points  $A$  and  $C$  are at the ends of a horizontal tube





altered and are neither uniform nor similar to what they were before heating. Consequently the expansion of the glass before being worked does not accurately represent the behaviour of the finished vessel. An attempt to get over this has been made, in which the bulb was made from a long piece of glass tube of which the coefficient of linear expansion was determined and the end then sealed. Although this is fairly accurate the better method for all ordinary work is to standardize a vessel by using Regnault's values for mercury.

**Silica Vessels.**—The cubical expansion of silica is only about 1 per cent. that of mercury; a determination, of the expansion of mercury in a silica vessel can be corrected for the expansion of the vessel, and if the latter had an error of as much as 10 per cent. it would only mean an error of 1 in 1000 in the value of the coefficient for mercury. It is not likely that the error would be as much as 10 per cent. if the expansion of the vessel were deduced from a measurement of the linear expansion of a sample of silica by the same maker.

## CHAPTER VI

### EXPANSION OF GASES

The measurement of the expansion of gases differs from that of the expansion of liquids and solids in one important particular. We can say that a given liquid or solid has a certain volume at any one temperature, but in the case of a gas such a statement would have no meaning. For a gas will fill any vessel into which it is put; if the volume of the vessel is increased the gas continues to fill it, but does not exert so great a pressure on the walls. In the same way, if the volume is diminished, the gas is compressed and exerts a greater pressure. Whenever, then, the volume of any quantity of gas is to be measured, we must take into account the pressure in order that our measurement may have any meaning. It will be convenient to consider the connection between pressure and volume before dealing with the changes due to rise in temperature.

The subject was investigated by Boyle in 1662. The principle of his experiments was to take a quantity of gas and compress it, and note the pressure when the volume was halved. He found that at this stage the pressure was double that at which the experiment started. He then continued until this new volume was again halved, and found that at this stage the pressure was again doubled and so on. These results are summed up in the statement known as Boyle's Law (sometimes known as Marriotte's Law): "At constant temperature, the pressure exerted by any given mass of gas is inversely proportioned to the volume."

This Law may be conveniently studied by means of the apparatus shown in Fig. 34. A stout glass tube AB is fitted

at the upper end into a pressure gauge, and at the lower end into an iron tube BC bent into a U. The end C is closed by a removable screw cap fitted with an ordinary bicycle tyre valve. The pressure gauge is graduated to read the "absolute" pressure in pounds per square inch, i.e. when exposed to ordinary atmospheric pressure it reads just under 15 lb. per square inch.

The cap C is removed, and water poured into the tube BC; the water should practically fill the part BC. In this way a quantity of air is enclosed in the tube AB. The cap C is then replaced.

By means of an ordinary bicycle pump the water in CB can be driven down, compressing the air in AB. The tube is graduated to show the volume of this air, and the pressure is given by the gauge. A series of readings are taken and entered in tabular form thus:—

Volume of Air cubic inches.	Pressure pounds per sq. inch.	Pressure $\times$ Volume.

Now if Boyle's Law represents the facts, the pressure should vary inversely as the volume, i.e. :—

$$P \text{ should vary as } \frac{1}{V}$$

$$\text{or } P \div \frac{1}{V} \text{ should be constant}$$

i.e.  $P \times V$  should be a constant.

The last column will show the results obtained by multiplying the volume by the corresponding pressure in each case.

Another form of apparatus for the same purpose is shown in Fig. 35. It is much more like the apparatus used by

Boyle, and in the hands of a fairly skilled observer gives more accurate results than does the method of the preceding paragraph.

It consists of a glass tube AB closed at the upper end, and having a length of thick rubber tubing C attached to it.

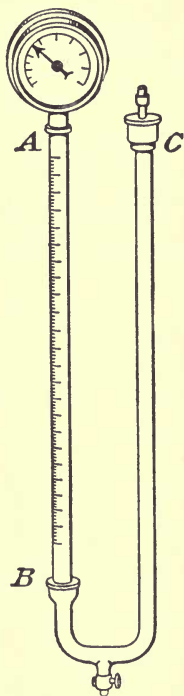


FIG. 34.

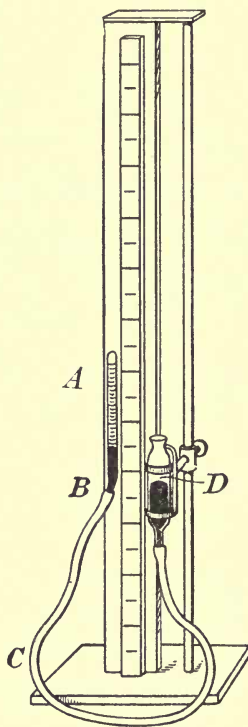


FIG. 35.

The other end of this rubber tube is attached to a glass tube D, open at the top and fastened to a block which can slide up and down the stand. The tube AB is graduated, and contains dry air or other gas. C is filled with mercury, which rises some way into D.

Starting with D near the bottom of the stand, the volume

of the air in AB is noted. The level of the mercury in D and in AB is noted on a vertical scale ; the difference between these two gives the difference between the pressure in AB and that of the atmosphere. This latter is obtained by reading the barometer. The pressure in AB is thus obtained by adding to the barometer reading the difference between the levels of the mercury in the two limbs (or subtracting this difference if the reading in D is below that in AB).

The block carrying D is then moved up a little way and readings taken again. In the same manner a series of readings is obtained and entered in tabular form thus :—

Vol. of gas.	Level of Mercury in AB.	Level in D.	Height of D above AB.	Pressure.	Pressure $\times$ Vol.

This method has the advantage that the pressure is measured in terms of a column of liquid (which is more accurate than a gauge) and the gas is dry ; on the other hand, it is not possible to reach such high pressures as in Fig. 34 without making the apparatus an unmanageable size.

It is now known that Boyle's Law is not strictly true for any gas, especially at high pressures. Gases like hydrogen, oxygen, air, etc., which are difficult to liquefy, obey the law very nearly indeed ; in the case of the easily liquefiable gases the departure from the law becomes considerable (see Chapter XVII).

**The Coefficient of Expansion of a Gas at Constant Pressure.**—To obtain a result comparable with the coefficients of expansion of solids and liquids we must ensure that the volume changes are due to changes of temperature



only ; in order to do this, the pressure of the gas must be kept constant throughout the measurements. A convenient laboratory method of determining the coefficient of expansion is as follows :—

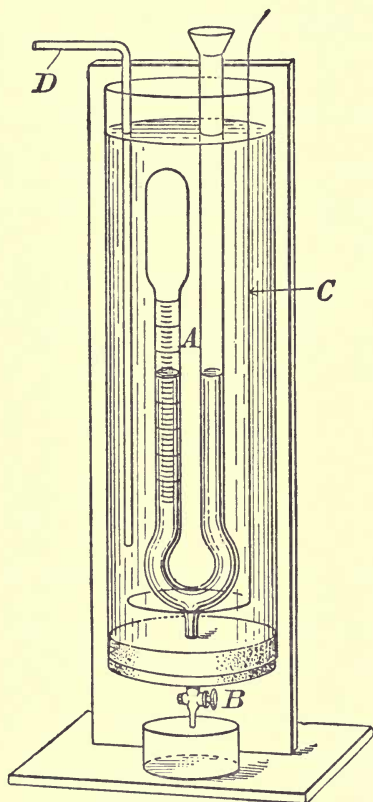


FIG. 36.

The closed limb of the U-tube A (Fig. 36) terminates in a bulb. Some air is confined in the bulb and part of the limb by concentrated sulphuric acid which serves the double purpose of indicating the pressure of the air and acting as a drying agent. The volume of the air is shown by graduations on the limb which read directly to .1 c.c. The U-tube is surrounded by a wide tube C which is filled with water, preferably cooled by ice to  $0^{\circ}$  C. The open end of A is above the water surface. The water is thoroughly stirred and sulphuric acid is poured into the open end of A or run out by the tap B until the level is the same in each limb. The volume of the air is read off. The water in C is then heated by blowing in steam

through D for a short time ; it is thoroughly stirred, acid is run out from B until the level in the two limbs is again the same, and the new volume of the air noted. A series of readings are taken at different temperatures, the acid in the two limbs being brought to the same level for each reading.

The following figures from an experiment illustrate what happens :—

Temperature.	Volume.
10·5° C.	28·45 c.c.
23° C. > 12·5	29·7 c.c. > 1·25
51° C. > 28	32·5 c.c. > 2·8
73° C. > 22	34·7 c.c. > 2·2

The readings may be plotted in the form of a graph ; examination of the particular values given shows that increase in volume per degree is constant and happens to come out as ·1 c.c. per degree.

To determine the volume at 0° C. we have—

$$\text{Change for } 10\cdot5^\circ = 1\cdot05 \text{ c.c.}$$

$$\text{Volume at } 0^\circ = 28\cdot45 - 1\cdot05 = 27\cdot4 \text{ c.c.}$$

$$\text{Coefficient} = \cdot 1/27\cdot4 = \cdot 00365.$$

We have neglected the expansion of the glass ; as the coefficient of cubical expansion of glass is about ·000025 it would only affect the last figure, and so for this sort of experiment may be left out. The apparatus has two great merits—the use of sulphuric acid (cp. page 83), and the fact that both surfaces of the acid are in the jacket.

Careful experiments on the coefficient of expansion of gases were made by Dalton and Gay Lussac, and later Regnault carried out a series of very accurate determinations. The results show that to a very close approximation the coefficient is the same for all gases,<sup>1</sup> being equal to ·00367 or  $\frac{1}{273}$ . This fact is known as Charles' Law (sometimes as Gay Lussac's Law) and may be stated thus : At constant pressure a gas expands  $\frac{1}{273}$  of its volume at 0° C. for each 1° C. rise in temperature.

**The Pressure Coefficient.**—If we heat a gas but do not allow it to expand, it is clear that the pressure will increase.

<sup>1</sup> Regnault gives the value for hydrogen as  $\frac{1}{273\cdot1}$  and for air as

$\frac{1}{272\cdot4}$

In this case we can measure the *coefficient of increase of pressure at constant volume*, by which we mean the fraction of its value at  $0^\circ \text{C}$ . by which the pressure increases for each degree rise in temperature. This coefficient is often referred to as the *pressure coefficient* and denoted by  $\beta$  to distinguish it from the coefficient of expansion at constant pressure, which is spoken of as the *volume coefficient* and denoted by  $\alpha$ .

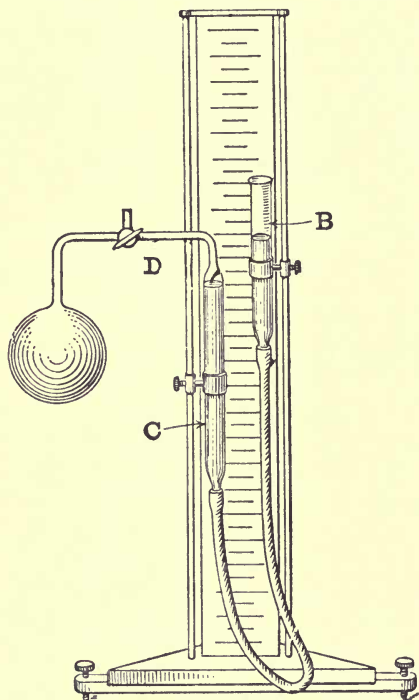


FIG. 37.

If the gas obeys Boyle's Law accurately  $\alpha$  and  $\beta$  are equal. For let the volume of the gas at  $0^\circ \text{C}$ . and pressure  $P_0$  be  $V_0$ . If the temperature be raised to  $T^\circ \text{C}$ . and the pressure kept constant the volume will become  $V$  where

$$V = V_0(1 + \alpha T) \quad (1)$$

If now the temperature be kept at  $T^\circ \text{C}$ . and the gas compressed until its volume is once more  $V_0$ , the new pressure  $P$  will be given by Boyle's Law equation

$$P_0 V = P V_0.$$

From (1) we have

$$P_0 V_0 (1 + \alpha T) = P V_0$$

$$\text{or } P_0 (1 + \alpha T) = P.$$

But if we had throughout kept the volume at

$V_0$  we should have had by definition of  $\beta$ .

$$P_0 (1 + \beta T) = P.$$

Thus

$$\alpha = \beta.$$

**Determination of  $\beta$  for Air.**—A convenient laboratory method is by means of the apparatus shown in Fig. 37.

The bulb is connected by a glass tube of small bore to the wider tube C which is connected by thick rubber tubing to B. B is carried by a block which can move up and down, in the same manner as the apparatus for verifying Boyle's Law described on pages 72 and 73. (That apparatus is in fact often provided with a separate bulb so that it can be used for this experiment as well as for Boyle's Law.) The bulb is filled with dry air, and is surrounded by melting ice. B is moved until the surface of the mercury in the left-hand limb is just level with the mark. The difference between the level of the mercury in B and C is noted on the scale; the pressure of the air in the bulb is thus obtained by adding (or subtracting if B is below C) this difference to the reading of the barometer. The bulb is then placed in a vessel containing water, which is maintained at the boiling-point. B is raised until the surface of the mercury in C is once more at the mark, and the difference in level is again noted. From these two readings the increase in pressure is obtained and  $\beta$  calculated, as shown in the following experiment:—

Barometer. 74.2 cms.

Temp.	Reading of Mercury at the Mark in C.	Reading of Mercury in Open Limb.	Difference in Height.	Pressure Cm. of Hg.
0° C.	18.0 cm.	18.3 cm.	+ .3	74.5
98.5° C.	18.0 cm.	44.7 cm.	+ 26.7	100.9

Increase in pressure for 98.5° C. = 26.4 cm. of mercury  
per degree = .268 cm.

$$\beta = .268/74.5 = .0036$$

In this experiment also the expansion of the bulb is neglected. The air in the tube D is also not at the same temperature as that in the bulb, but the correction for this is small as the tube can be of small diameter and therefore

the total volume of the air is small compared to that in the bulb, and in an ordinary laboratory experiment can be neglected.<sup>1</sup> There is, however, the error

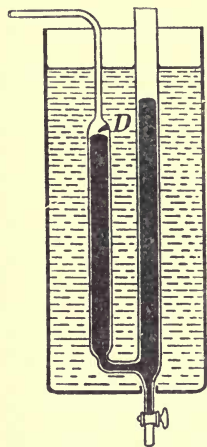


FIG. 38.

due to the fact that the mercury near D is at a different temperature from that in B and consequently has a different surface tension which produces a considerable error in a narrow tube (cp. page 66 on the absolute expansion of liquids).

For this reason in Regnault's experiments the manometer was arranged as shown in Fig. 38. The mark against which the mercury surface was maintained being the extremity of D, and the manometer being kept in a water bath, and the pressure adjusted by pouring in or running out mercury.

A correction for the small volume of air in the manometer and tube was made.

**Gas Thermometers.**—Gases such as air, hydrogen, or nitrogen, can be used as thermometric substances either by keeping the pressure constant and observing the volume change, or by observing the pressure necessary to keep the volume constant. The latter method is the more satisfactory, and the gas thermometers in actual use are almost invariably of the constant volume type. Fig. 39 shows the standard constant volume hydrogen thermometer at the Bureau International des Poids et Mesures.

Gas thermometers have certain great advantages. They are very sensitive, the change in pressure per degree being large, and moreover pressure is easily measured. They have also a great range of temperature, since hydrogen, for example, remains a gas down to very low temperatures, while the upper limit is practically fixed by the

<sup>1</sup> In the form supplied by many makers and used above the tube is very long and an appreciable error results.



material of the bulb. By using porcelain, temperatures up to  $1100^{\circ}$  C. can be determined. They have, however, certain disadvantages. In the first place they are necessarily rather large and cumbersome and can only be used in one position. In the second place, gases being bad conductors, a long time must elapse before the gas takes up the temperature of the substance with which the bulb is in contact. The occasions on which a gas thermometer could be used directly are in fact very rare; their great use is as a standard. The temperatures are measured in the first place by a mercury-in-glass thermometer or one of the electrical methods (see Chapter XVI) and the mercury thermometer or other instrument is calibrated by comparing it with the standard gas thermometer. This will be referred to again later (see Chapter XVI).

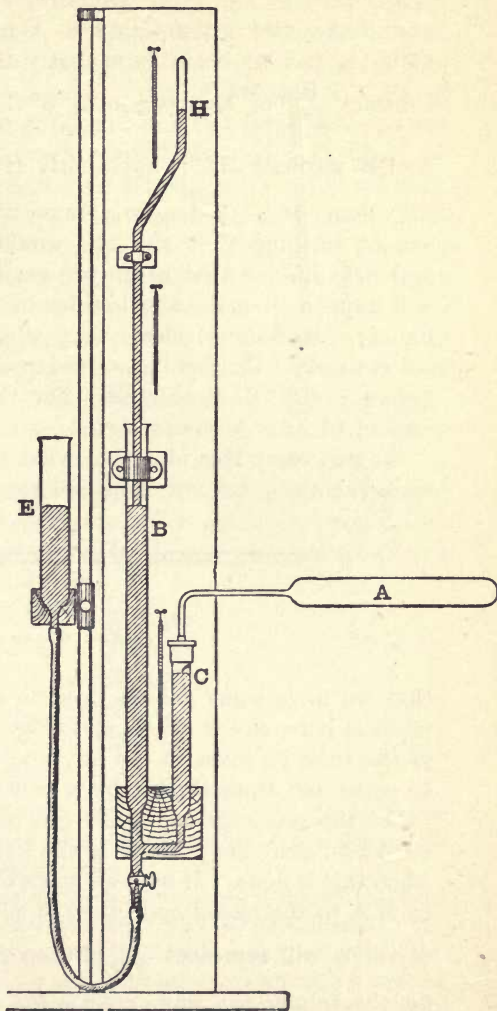


FIG. 39.

**Absolute Temperature on the Gas Scale.**—A gas at constant pressure expands  $\frac{1}{273}$  of its volume at  $0^{\circ}$  C. for each degree rise in temperature. Suppose we have some gas at  $0^{\circ}$  C., and we begin to cool it. If we cool it  $10^{\circ}$ , it will contract  $\frac{10}{273}$  of its volume at  $0^{\circ}$  C. Suppose we were to cool it through  $273^{\circ}$ ; apparently it would contract  $\frac{273}{273}$  of its volume at  $0^{\circ}$  C., i.e. its volume would be zero. Now we cannot imagine that the gas would disappear altogether, and so it follows that before we get to  $-273^{\circ}$  C. something will happen to make the law break down, e.g. the gas will liquefy. It follows, then, that whatever gas we use will cease to obey Charles' Law, and presumably become liquid before  $-273^{\circ}$  C. is reached. For this reason  $-273^{\circ}$  C. is spoken of as "Absolute zero."

We can carry this idea somewhat further with very useful consequences. Let us imagine, for the sake of clearness,

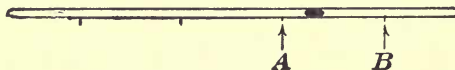


FIG. 40.

that we have some gas enclosed in a long straight tube of uniform bore, closed at one end (Fig. 40). Let the other end of the tube be open to the air, and let the gas in the tube be separated from the air by a pellet of some liquid.

Let the temperature of the gas be brought to  $0^{\circ}$  C., and let A represent the position of the left-hand edge of the pellet when this is done. If now we mark off the length of the tube from A to the closed end into 273 equal parts, each of these divisions will represent  $\frac{1}{273}$  of the volume of the gas at  $0^{\circ}$  C., i.e. the volume the gas expands for each degree centigrade. Now mark off 100 such divisions to the right of A and let

the hundredth division be at B. The arrangement now constitutes a kind of constant pressure gas thermometer and each division corresponds to  $1^\circ$ . If we want it to read centigrade degrees, we must number A 0 and B 100, because on the centigrade scale the melting-point of ice is taken as the starting-point and called zero. But if we had a scale of temperature in which each degree had the same value as the centigrade degree but which started at  $-273^\circ\text{C}$ ., then we could make our thermometer read temperatures on this scale by numbering the divisions from the closed end of the tube, so that A would be  $273^\circ$  and B  $373^\circ$ . This scale is called the *absolute scale* and, as will be seen, the volume of the gas is proportional to its "absolute temperature."

The absolute scale, then, is the centigrade scale starting from  $-273^\circ\text{C}$ . so that  $10^\circ\text{C} = 283^\circ\text{A}$ , and Charles' Law may then be written: "The volume of any gas is proportional to its absolute temperature so long as the pressure remains constant."

The absolute scale simplifies calculations of the volume of a gas at different temperatures. For example, suppose we have collected 500 c.c. of gas at  $15^\circ\text{C}$ . and we require to know what it would occupy at  $0^\circ\text{C}$ .

$$15^\circ\text{C} = 288^\circ\text{A}.$$

$$0^\circ\text{C} = 273^\circ\text{A}.$$

$$500 \text{ c.c. : volume at } 0^\circ\text{C. as } 288 : 273,$$

$$\text{or volume at } 0^\circ\text{C.} = 500 \times \frac{273}{288} \text{ c.c.}$$

$$= 474 \text{ c.c.}$$

**Regnault's Determination of  $\alpha$ .**—Regnault adopted several methods, of which the one described in outline below proved on the whole to be most satisfactory.

A bulb A (Fig. 41) was connected by means of capillary tubing B to a manometer CE, of which the limb C was graduated. The manometer contained mercury. The bulb was filled with carefully dried air (see page 83) and was then surrounded by melting ice. Mercury was poured into the limb E of the manometer until the surfaces in C and E were at the same level as shown. The bulb

was then surrounded by steam; the air expanding pushed the mercury down in C and up in E. By opening the tap D mercury was run out until the surfaces were once more level in some position lower than C. The volume of the bulb and capillary tube had been previously determined, and the expansion is given by the difference in the two readings on C.

Two corrections are necessary. In the first place, the air in the part C of the manometer (and in the part of B not in contact with the ice or steam) is not at the same temperature as that in

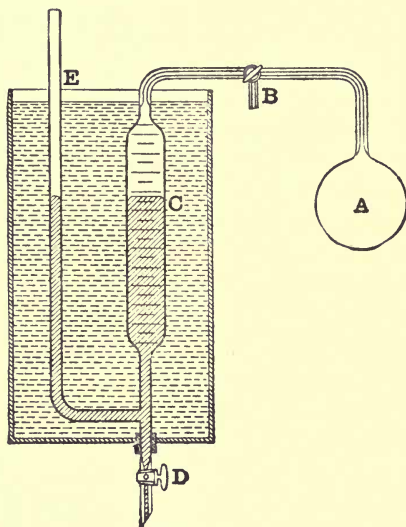


FIG. 41.

the bulb. The volume of the air in B is small, but the amount in C between the two positions is quite large, about one-third of the volume of the bulb. In the actual experiment the manometer was kept in a water bath and the temperature noted. The quantity of air was also adjusted so that the first position of the mercury surface was in the narrow tube. The other correction is for the expansion of the bulb and tube.

The great difficulty in all experiments on the expansion of gases is to get rid of the film of moisture which is present on the interior walls of the containing vessel, and if this be not done, the

moisture becomes partly converted into vapour when heated, and makes the gas appear to expand more than it really does ; for this reason the earlier values of the coefficient were too high. In order to dry the bulb it is alternately exhausted and filled with dry air, the process being repeated many times, and the bulb continually gently heated.



## CHAPTER VII

### HEAT AND ITS MEASUREMENT

In Chapter I it was stated that we have the idea of something being communicated to a body when it becomes hotter or given out by the body when it becomes colder, and that to this "something" we give the name heat. We must now follow up this idea, and we shall see that heat is a quantity capable of definite measurement. For this purpose it will be convenient to start with a source of heat and consider some of its effects. A gas-burner is one source, but it will be much easier to take an electric heater of the immersion type, such as is sometimes sold for heating shaving water, etc. We can put this in liquids and see what it is doing; the experimental difficulties in the case of a gas-burner are much greater (see page 89).

To get an idea of the power of the heater, suspend it in a beaker containing a known mass of water. Switch on the current and note the temperature of the water every half-minute; the water must be well stirred all the time, otherwise the observed temperature will depend on the position of the thermometer. Continue until the temperature is about  $50^{\circ}$  C. The following results of an experiment <sup>1</sup> will illustrate the effect:—

<sup>1</sup> The heater used was an ordinary domestic immersion heater by the G.E.C., working on a 220 volt circuit and taking about 1.5 ampères.

Mass of water 830 gms.

Crude alcohol, mass 830  
gms. (volume = 1,000 c.c.)

Time (minutes).	Temperature.
0	16.5° C.
	1
$\frac{1}{2}$	17.5° C.
	2
1	19.5° C.
	2.5
$1\frac{1}{2}$	22° C.
	3
2	25° C.
	3
$2\frac{1}{2}$	28° C.
	3
3	31° C.
	2.5
$3\frac{1}{2}$	33.5° C.
	3
4	36.5° C.
	3
$4\frac{1}{2}$	39.5° C.
	3
5	42.5° C.
	3
$5\frac{1}{2}$	45.5° C.
	2.5
6	48° C.
	3
$6\frac{1}{2}$	51° C.
	2.5
7	53.5° C.

Time (minutes).	Temperature.
0	16.5° C.
	1
$\frac{1}{2}$	17.5° C.
	3
1	20.5° C.
	5
$1\frac{1}{2}$	25.5° C.
	3.5
2	29° C.
	4
$2\frac{1}{2}$	33° C.
	4
3	37° C.
	4
$3\frac{1}{2}$	41° C.
	3
4	44° C.
	4
$4\frac{1}{2}$	48° C.
	3.5
5	51.5° C.

It will be noticed that after the first minute <sup>1</sup> the rate of rise of temperature is practically constant, being just under 6° per minute on the average. If the experiment be repeated with the same heater and beaker, but using an equal mass of alcohol instead of water, it will be found that although

<sup>1</sup> At the start the current has to raise the temperature of the coils and container of the heater before it can communicate heat to the water.

the volume of alcohol is greater, the rate of rise in temperature is greater. Table 2 gives the results of such an experiment. In the interval of time from the first minute to the fifth the temperature of the water is raised from  $19.5^{\circ}\text{C}$ . to  $42.5^{\circ}\text{C}$ ., i.e. through  $23^{\circ}$ . In the similar interval the temperature of the alcohol is raised from  $20.5^{\circ}\text{C}$ . to  $51.5^{\circ}\text{C}$ ., i.e. through  $31^{\circ}\text{C}$ . Now there is no reason to suppose that there is any large difference between what the heater supplies in one interval of four minutes and the other four minutes. But it is clear that we cannot give any idea of what the heater has done by saying that in four minutes the heater raises the temperature of liquid by so many degrees unless we know what kind of liquid was used and how much. But if this information is supplied the method can be adopted, and quantities of heat are expressed in this way. The liquid fixed upon as a standard is water, and a unit of heat is defined as the amount of heat required to raise the temperature of unit mass of water  $1^{\circ}$ . Since there are more than one scale of temperature and more than one unit of mass there are several units of heat in use. For scientific work the unit of heat is the *calory*, which is defined as the amount of heat required to raise the temperature of 1 gramme of water  $1^{\circ}\text{C}$ .<sup>1</sup> A unit sometimes met with, especially in works on chemistry, is the large or kilogram calory, the amount of heat required to raise the temperature of 1 kg. of water  $1^{\circ}\text{C}$ . Two other units are used by engineers in this country, i.e. *The British Thermal Unit* (B.Th.U.), the amount of heat required to raise the temperature of 1 lb. of water  $1^{\circ}\text{F}$ .; *The Thermal Unit* (T.U.), the amount of heat required to raise the temperature of 1 lb. of water  $1^{\circ}\text{C}$ .

Thus, in our experiment, the heater in four minutes was

<sup>1</sup> Strictly speaking, the amount of heat required to raise the temperature of 1 gm. of water  $1^{\circ}\text{C}$ . varies slightly at different parts of the scale. In accurate work this is allowed for, and the part of the scale specified in the definition (see Chapter VIII, page 128). For ordinary work the difference can be neglected. In the case of some liquids (notably alcohol) there is an appreciable difference in the amount of heat required to raise the temperature of 1 gm.  $1^{\circ}\text{C}$ . at different parts of the scale.

able to raise the temperature of 830 gms. of water  $23^{\circ}$  C. We can say, therefore, that it supplied to the water  $23 \times 830 = 19,090$  calories in this time, or an average of 4,773 calories per minute. Experiments of this type are the basis of the method of determining the heating value of fuels (see page 89).

**Thermal Capacity.**—The thermal capacity of any object is the amount of heat required to raise its temperature  $1^{\circ}$ . For example, the beaker full of alcohol had its temperature raised  $31^{\circ}$  C. by the heater in four minutes. But the experiment with the water showed that in four minutes the heater supplies about 19,090 calories. Hence the beaker of alcohol requires 19,090 calories to raise its temperature  $31^{\circ}$ .<sup>1</sup> We should therefore say that the thermal capacity of the beaker of alcohol was 616 calories. We sometimes speak of the thermal capacity of a substance; in this case it is understood to mean unit mass of it. Thus we should say that the thermal capacity of our alcohol (since we had 830 gms. of it) was  $\frac{616}{830}$  or .74 calories per gramme.

**Specific Heat.**—It is more usual to deal with the Specific Heat of a substance. This is defined as the ratio of the thermal capacity of any mass of the substance to the thermal capacity of an equal mass of water, or in other words, Specific Heat of a substance is equal to—

Heat required to raise the temperature of any mass of it  $1^{\circ}$

Heat required to raise same mass of water  $1^{\circ}$

It should be noted that the Specific Heat is a number and does not depend on the units of heat or of mass employed. If the unit of heat is the calory, the Specific Heat is numerically equal to the thermal capacity of 1 gm. of the substance; for example, the Specific Heat of the alcohol of our experiment is given by—

<sup>1</sup> Since the thermal capacity of a mass of alcohol varies considerably with the temperature, the 616 calories represents the average thermal capacity over a range  $20^{\circ}$  C.— $51^{\circ}$  C. The specimen of alcohol used was very impure.

$$\frac{\text{Thermal capacity of the alcohol}}{\text{Thermal capacity of the same mass of water}} = \frac{616}{830} = .74$$

There are, however, some units of heat not defined in terms of water (e.g. work units as explained in Chapter VIII), and if these are used the numerical value of the thermal capacity will not be equal to the Specific Heat. Specific Heat must always be defined as a ratio, and not as a quantity of heat. The distinction is rather like that between Specific Gravity and Density.

Hitherto we have been dealing with liquids, but solids also vary to an even greater extent in their thermal capacities.

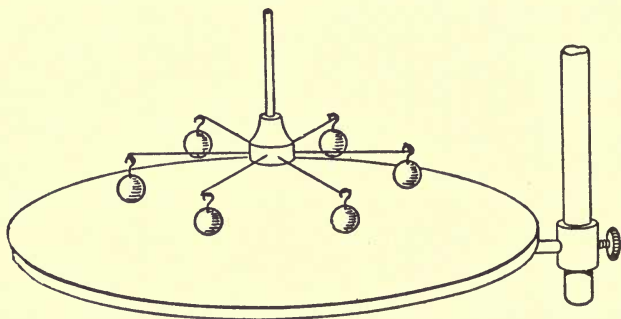


FIG. 42.

The following experiment is a rough illustration of this (Fig. 42).

A number of spheres of the same size, but made of different metals, such as copper, tin, lead, are provided with hooks so that they can be hung from the arms of a handle of the shape shown in the figure. By this means they are suspended in a vessel of boiling water and left there for some time. They are then lifted out by the handle and placed on a sheet of paraffin wax carried on the ring of a retort stand; the handle is disengaged by a slight turn and removed. The spheres give out heat as they cool and melt some of the wax with which they are in contact: they therefore sink into the wax. This goes on until the spheres have cooled below the



melting-point of the wax. It will be found that the spheres have got to very different depths; if the wax is of suitable thickness<sup>1</sup> the copper sphere will melt its way right through and fall down, the tin will be partly through and the lead will make very little impression. It should be noted that the spheres are of equal size and not of equal mass; to compare specific heats we ought to have taken equal masses, in which case the lead would have been smaller and the difference in behaviour between it and copper would have been more marked.<sup>2</sup>

**Calorimetry.**—Operations involving the measurement of quantities of heat are classified under the general term calorimetry, and any apparatus for making such measurements is called a calorimeter. In the simplest forms the calorimeter is a vessel of suitable material containing a known mass of water, to which the heat is communicated.<sup>3</sup> The quantity of heat is measured by observing the rise in temperature of the water as in the case of the electric heater; there are, however, certain corrections to be considered. The main principles may be illustrated by a brief account of an operation of great practical importance—the determination of the calorific value of fuels. The calorific value of a fuel is the amount of heat given out when a definite weight, 1 lb. or 1 kg., is burnt; in the cases of gaseous fuels the value is usually given as so many units of heat per cubic foot or per cubic metre.

**Determination of the Calorific Value of a Fuel such as Coal.**—The practical difficulty is to make sure that all the heat given out by the fuel is accounted for. One method

<sup>1</sup> With spheres about 1 inch in diameter the sheet of wax should be about  $\frac{1}{4}$  inch thick or a little more.

<sup>2</sup> In all cases of heat measurement we are concerned with masses, not volumes. The volume of any given substance depends on its temperature and, at any rate in the case of gases, on the pressure. The mass does not depend on these conditions and so gives us a constant quantity with which to work.

<sup>3</sup> Other types of calorimeter are dealt with at the end of Chapter X, see page 167.

is to use a bomb calorimeter (Fig. 43). A known weight of the coal, which has been powdered and dried, is placed in a small capsule inside a strong steel shell or bomb; this bomb has a gas-tight cover, fitted with a valve. The cover is put

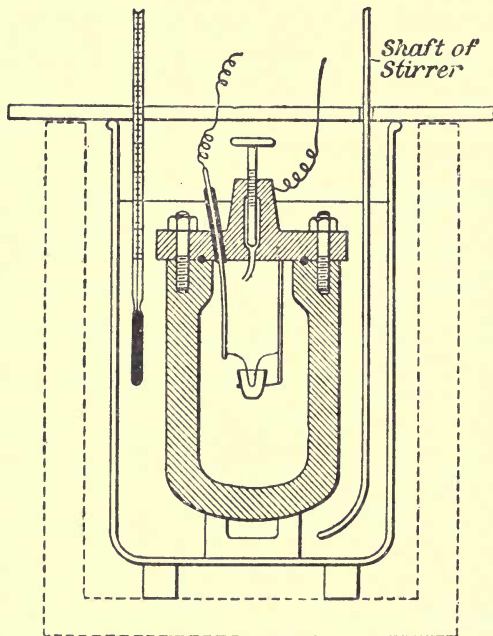


FIG. 43.

on, and oxygen is admitted through the valve until the bomb is filled with oxygen under a suitable pressure.<sup>1</sup> The bomb with its contents is immersed in a known weight of water contained in a metal calorimeter. This calorimeter is surrounded by a water-jacket shown by the dotted lines. The temperature of the water in the calorimeter is determined by a thermometer which should read to  $\frac{1}{100}^{\circ}$  C. and care is taken

<sup>1</sup>The pressure depends on the amount of fuel and the size of the bomb. A usual size is to have a bomb of about 600 c.c. capacity, in which case about 1 gm. of coal would be used, and the pressure of the oxygen would be about 25 atmospheres

that the calorimeter, bomb and water are at the same temperature ; this is done by keeping the water well stirred and reading the thermometer every minute until the temperature is constant. The fuel is then ignited by passing an electric current through a fine platinum wire lying in contact with the coal and connected to terminals on the outside of the bomb. The wire becomes red hot and the fuel then burns completely in the excess of oxygen, the products of combustion remaining in the bomb.<sup>1</sup> The water in the calorimeter is thoroughly stirred and the highest temperature reached is noted.

The heat given out by the burning coal has raised the temperature of the known mass of water through a certain range, but in addition to this the bomb and the calorimeter (and also the stirrer and thermometer) have been raised through this same range ; the effect of the stirring was to make sure that they all started at the same lower temperature and that they all finished at the same higher temperature. A correction must therefore be applied to allow for the fact that these things were heated as well as the water ; in order to find the amount of heat given by the coal we must multiply the rise in temperature by the mass of water + the water equivalent of the calorimeter, bomb, etc. By the *water equivalent* of any object we mean the mass of water which requires as much heat to raise its temperature 1° as is required to raise the temperature of the object 1°, or, in other words, the amount of water which has the same thermal capacity as the object.

Thus, suppose that the calorimeter contained 2,500 gms. of water, the initial temperature was 18.92° C., and the final temperature was 20.80° C. Let us suppose that the water equivalent of the whole apparatus was known to be 700 gms. Then heat given out by the coal =

$$(2,500 + 700) (20.80 - 18.92) = 3,200 \times 1.88 \text{ calories.}$$

The water equivalent can be determined by a direct ex-

<sup>1</sup> The products of combustion would have a corrosive action on steel, so the inside of the bomb must be protected by a lining of enamel or else of platinum or gold.

periment (see page 97) ; it is, however, possible to calculate the water equivalent of any vessel if its mass and the specific heat of the material are known. For if  $m$  is the mass and  $x$  the Specific Heat, we have—

Thermal capacity of the vessel =  $x$  times thermal capacity of  $m$  gms. of water.

= thermal capacity of  $xm$  gms. of water.

∴ water equivalent of vessel =  $xm$  gms.

or water equivalent of any vessel = mass of vessel  $\times$  Specific Heat of the material.

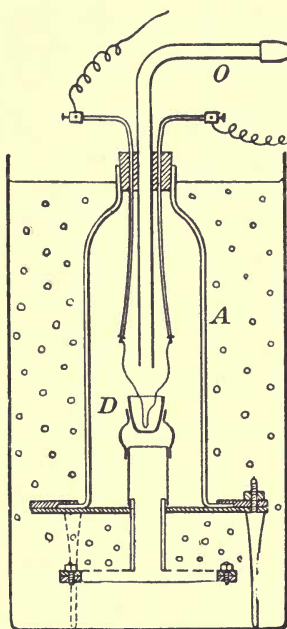


FIG. 44.

Bomb calorimeters are expensive, and a much cheaper instrument which can be made to give good results is Darling's calorimeter, Fig. 44. The coal is contained in a nickel crucible  $D$ , and the combustion takes place under a kind of bell jar  $A$ , which is immersed in the water. Oxygen is admitted through the tube  $O$ , and bubbles out together with the products of combustion through openings at the base. The issuing gases communicate their heat to the water and also help to stir it. The writer gets very satisfactory results with this calorimeter, but a little practice

in regulating the oxygen is usually necessary to be sure of success.

#### Determination of the Specific Heat of a Solid.

The most straightforward methods are those which may

be classified under the general term of the "method of mixture." The simplest form of it, which we shall now consider, is rather rough, but gives quite satisfactory results to an accuracy of 5 to 10 per cent. It is suitable only for metals.

A lump of metal (some 500 to 800 gms.), preferably in the form of a thick disc, is provided with a wire handle. It is first weighed to the nearest gramme and then placed in a saucepan of water heated on a ring burner. A copper<sup>1</sup> calorimeter is weighed empty, then about two-thirds filled with water and weighed again. It is then placed on three corks (to avoid as much as possible conduction of heat to the bench), and the temperature of the water is noted. When the lump of metal has been in the boiling water of the saucepan for some time (5 or 10 minutes) it is lifted out by the wire handle, given a quick shake and transferred as rapidly as possible to the calorimeter and immersed in the water. The water is well stirred (by moving the lump of metal) and the highest temperature noted.

It will be convenient to follow out the method of calculation by using some figures from an actual experiment.

Weight of metal lump . . . . .	427 gms.
Weight of calorimeter empty . . . . .	192 gms.
Weight of calorimeter + water . . . . .	<u>710 gms.</u>
∴ Weight of water . . . . .	<u>518 gms.</u>
First temperature of water . . . . .	$\overline{15.5}^{\circ}\text{C.}$
Final temperature of water . . . . .	$19.0^{\circ}\text{C.}$

The lump of metal cooled through a certain range of temperature, i.e. from  $100^{\circ}\text{C.}$  down to  $19^{\circ}\text{C.}$ , this latter being the final temperature of both metal and water. In doing this it gave out heat, and this heat was measured in just the same way as in the case of the fuel, i.e. by finding its effect on a known mass of water in a calorimeter.

<sup>1</sup> Calorimeters are usually made of copper, but aluminium is also suitable.



The heat given out by the metal raised the temperature of the water and calorimeter from  $15.5^{\circ}\text{C}$ . to  $19^{\circ}\text{C}$ .

$\therefore$  Heat gained by calorimeter and water—

$$= (518 + \text{water equiv. of cal.}) \times (19 - 15.5) \text{ calories.}$$

The water equivalent of the calorimeter may be got either by direct experiment or by assuming the Specific Heat of copper. This latter is about  $.1$  (strictly  $.095$ ), so that the water equivalent of the calorimeter is  $.1 \times 192$  or about  $19$  gms.

$\therefore$  Heat gained by calorimeter and water

$$= (518 + 19) \times 3.5 = \text{calories}$$

$$= 537 \times 3.5 \text{ calories.}$$

Now this heat was supplied by the metal in cooling from  $100^{\circ}\text{C}$ . down to  $19^{\circ}\text{C}$ ., i.e. through  $81^{\circ}$ .

Turning now to the metal; if  $S$  is its Specific Heat, the amount of heat given out by the  $427$  gms. of metal cooling  $1^{\circ}\text{C}$ . is  $S$  times that given by  $427$  gms. of water cooling  $1^{\circ}\text{C}$ . That is to say,  $427 \times S$  calories.

$\therefore$  Amount of heat given out by the metal in cooling through  $81^{\circ}$  would be—

$$427 \times 81 \times S \text{ calories.}$$

But as actually measured by the calorimeter it was found to be  $537 \times 3.5$  calories.

$$\therefore 427 \times 81 \times S = 537 \times 3.5$$

$$S = \frac{537 \times 3.5}{427 \times 81} = .054.$$

The above method is rather rough; two weak points are:—

(1) A certain amount of hot water is carried over with the metal in transferring it from the saucepan to the calorimeter.

(2) The metal is cooling as it is being transferred, so that its temperature is not  $100^{\circ}\text{C}$ . as it is placed in the calorimeter. It is not, however, so rough as it might appear at first sight, provided that considerable masses of metal are used; in the case considered the errors involved by (1) and (2) were small in comparison with the total quantities of heat involved. Incidentally (1) tends to make the final result too high, and

(2) tends to make it too low, so that we are concerned with the difference of these two effects and not their sum.<sup>1</sup> But the result depended on a temperature difference of  $3.5^{\circ}\text{C}$ ., and with a thermometer graduated in degrees this was the most uncertain part; it would have been a waste of time to try and eliminate (1) and (2) unless a more accurate temperature measurement was possible.

In more accurate work the substance must be heated in some form of heater in which it does not come in contact with water or steam, and arrangements are made for quick transference to the calorimeter. A very simple method, suitable for a fairly rough laboratory determination of the Specific Heat of a solid which is in the form of small pieces (e.g. copper turnings, iron nails, etc.), is to place the substance in a glass boiling tube which is placed in a saucepan of boiling water or passed through a large cork resting on the neck of a metal can so that the tube is in the steam of boiling water. The mouth of the tube is lightly plugged with cotton wool, and a thermometer is placed with its bulb well covered by the fragments of the substance. The tube is heated for a considerable time until the thermometer reading is constant. The tube is then removed, the plug of cotton wool taken out, and the contents quickly poured into the calorimeter. Various forms of steam heaters are sold, in which the substance can be poured out of its tube without removing the tube. Fig. 45 shows a more elaborate arrangement, due to Regnault.<sup>2</sup>

The substance is placed in a small wire gauze basket,

<sup>1</sup> By choosing a suitable size and shape for the lump of metal it is possible to ensure that the two errors very nearly neutralize one another on the average of a number of experiments. The figures quoted were from experiments with an apparatus of a suitable size, and the writer has made many experiments on the magnitude of this error. This must not be regarded as converting the method into an accurate one, but merely as indicating what are suitable dimensions. The experiments were undertaken to find out why the results obtained with a rough apparatus were consistently so close to the accepted values. But the experiments showed that the errors were fairly small, so that the method is quite good enough for work in which an ordinary thermometer is used, graduated in degrees.

<sup>2</sup> *Ann. de Chimie et de Physique*, 1840, 2<sup>e</sup> Ser., tom. 73.

suspended by a thread in the centre of a steam heater. This central space is closed at the top by a cork and at the bottom by a sliding shutter *A*. When the substance has been at its steady temperature for some time (e.g. half an hour), the

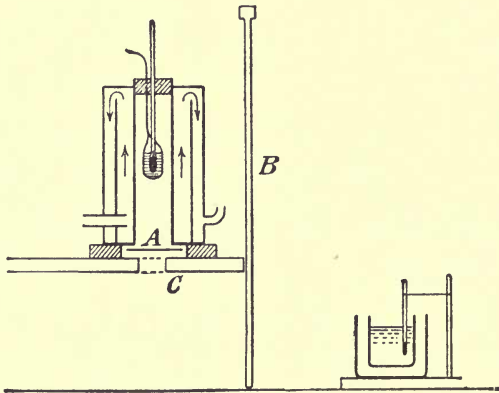


FIG. 45.

screen *B* is raised, the calorimeter is pushed under the heater and the substance quickly lowered into it; the calorimeter is then quickly withdrawn. The double-walled screen *C*, through which cold water circulates, protects the calorimeter from radiation from the heater.

**Errors Due to Cooling.**—We have assumed that the whole of the heat given out by the substance is measured by the rise in temperature of the water multiplied by the mass of water + water equivalent of the calorimeter. But as soon as the water becomes hotter than its surroundings it begins to lose heat and consequently the final temperature is lower than it ought to be. To minimize this effect in our rough experiment the calorimeter stood on three corks; it can be made very much less by suspending the calorimeter in a larger vessel so that there is an air space all round it, and by having the outside of the calorimeter and the inside of the outer vessel highly polished (see Chapter XIV). In this case, if the

rise in temperature of the water is only  $3^{\circ}$  or  $4^{\circ}$  the cooling effect is small, but in very accurate work it must be allowed for. The method of correction is given on page 114. It is sometimes recommended that the space between the vessels should be filled with cotton wool or felt, but although this helps to diminish the cooling it introduces great uncertainties in the corrections and should not be done.

**Direct Determination of the Water Equivalent of a Calorimeter.**—A simple method is to weigh the empty calorimeter and leave it for some time with a thermometer in it, to allow it to take up the temperature of the room. Some water, at a temperature of about  $25^{\circ}$  C. or  $30^{\circ}$  C., is got ready and its temperature carefully taken with an accurate thermometer. It is then immediately poured into the calorimeter until the latter is about two-thirds full. As soon as it is in the water is well stirred and its temperature taken with the same thermometer which was used before. The calorimeter and its contents are then weighed, to determine how much water was put in. The following figures may be used to illustrate the calculation :—

Weight of calorimeter empty . . . .	192 gms.
Weight of calorimeter + water . . . .	660 gms.
.∴ Weight of water . . . .	<u>468 gms.</u>
First temperature of calorimeter . . . .	$16.5^{\circ}$ C.
First temperature of water . . . .	$25.9^{\circ}$ C.
Final temperature of water . . . .	$25.55^{\circ}$ C.

Heat lost by water =  $.35 \times 468 = 164$  calories.

This heat raised the temperature of the calorimeter from  $16.5^{\circ}$  C. to  $25.55^{\circ}$  C., i.e. through  $9.05^{\circ}$ .

Therefore to raise the temperature of calorimeter  $1^{\circ}$  requires

$$164/9.05 = 18 \text{ calories.}$$

.∴ calorimeter is equivalent to 18 gms. of water.

It should be noticed that since the measurement is based on a fall of temperature of about  $.35^{\circ}$  C., the thermometer must read to at least  $.05^{\circ}$  in order to get an accuracy of anything like 10 per cent. The thermometer used was

graduated in  $\frac{1}{10}^{\circ}$ , and could easily be read to half this. Moreover if the water were much above  $30^{\circ}$  C. the fall in temperature due to ordinary cooling during the time of the experiment would be nearly as much as that due to the calorimeter; it is found by experiment that if it is not above about  $25$  to  $30^{\circ}$  C. the cooling is negligible in the short time taken by the experiment.

### Specific Heat of Liquids.

The method of mixtures can be applied in two ways. The liquid can be placed in a calorimeter and a solid of known specific heat can be heated and dropped in as already described. Another method is to place a known mass of the liquid in a thin metal container and heat this in a heater; the container with the liquid is then dropped into water in a calorimeter as in the case of a solid. In this case the thermal capacity of the container must be determined separately.

**Specific Heat by the Method of Cooling.**—This method gives fairly reliable results in the case of liquids.<sup>1</sup> It depends on the principle that if we have a closed vessel at a higher temperature than its surroundings it will lose heat by conduction, convection and radiation (see Chapter XII); the rate of loss of heat will depend on the area and nature of the surface and its temperature, and on the external conditions, but will not depend on what is inside it. The idea is therefore to measure the time taken to fall through a given range of temperature first when the vessel is full of water and then when it is full of the liquid. Since the mean temperature is the same in each case, the rate of loss of heat (calories per second) will be the same, but as the thermal capacities of the contents of the vessel are different the rate of fall of temperature (degrees per second) will be different.

The experimental arrangements are concerned chiefly in securing (1) that all parts of the liquid are constantly brought in contact with the walls of the vessel (otherwise the temperature of the liquid will not be closely related to that of

<sup>1</sup> Attempts to use this method for solids, in the form of powder tightly packed, were not satisfactory. Cp. Regnault.



the vessel), this involves adequate stirring; (2) that the cooling conditions are the same in each case.

A very convenient laboratory method is to make use of the Callendar apparatus for determining the mechanical equivalent of heat (see page 111).

Some water is heated to a temperature of about 30° C.,<sup>1</sup> and 250 c.c. are introduced into the brass drum; the special bent thermometer (which reads in fifths of a degree) is inserted and the drum (without its silk belt) is rotated by the motor at about 100 to 120 r.p.m. The time taken for the temperature to fall through a certain range is noted, e.g. from 25° C. to 20° C., readings being taken at each degree. The drum is then stopped, the water emptied out and 250 c.c. of the liquid (previously heated to about 30° C.) put in. The drum is then started up and the time taken for the temperature to fall through the same range noted. If there is time, the experiment can be repeated with water or alcohol as a check on the constancy of the cooling conditions. The following figures from an experiment will illustrate the procedure.

## Alcohol.

Temp.	Time.	Time Interval for 1°.	
		m.	s.
25° C.	h. m. s. 5 40 45	}	1 20
24°	5 42 5		1 40
23°	5 43 45	}	1 45
22°	5 45 30		2 10
21°	5 47 40	}	2 15
20°	5 49 55		

## Water.

Temp.	Time.	Time Interval for 1°.	
		m.	s.
25° C.	h. m. s. 6 36 0	}	2 50
24°	6 38 50		3 20
23°	6 42 10	}	3 50
22°	6 46 0		4 30
21°	6 50 30	}	4 55
20°	6 55 25		

<sup>1</sup> The thermometer supplied with the apparatus usually reads up to 30° C.; the water must therefore be heated not much above this temperature. It will be cooled a little as it is put in.

# HEAT

## Alcohol.

Temp.	Time.	Time interval for 1°.
25° C.	h. m. s. 7 33 35	m. s. 1 25
24°	7 35 0	1 40
23°	7 36 40	1 45
22°	7 38 25	2 5
21°	7 40 30	2 25
20°	7 42 55	

Water equivalent of drum = 39 gms. (see page 115).

Density of the alcohol = .83 gms. per c.c.

Taking the mean of the two sets of figures for alcohol, we have—

Temp. Range.	Time (seconds).	
	Alcohol.	Water.
25° 24°	82.5	170
24° 23°	100	200
23° 22°	105	230
22° 21°	127.5	270
21° 20°	140	295

$$\left. \begin{array}{l}
 \frac{170}{82.5} = 2.06 \\
 \frac{200}{100} = 2.00 \\
 \frac{230}{105} = 2.19 \\
 \frac{270}{127.5} = 2.11 \\
 \frac{295}{140} = 2.10
 \end{array} \right\} \begin{array}{l} \text{Mean} \\ = 2.1 \\ \text{nearly.} \end{array}$$

Taking any of these temperature ranges, say 25° to 24°, the heat given out when the drum contains water is—

$$(250 + 39) = 289 \text{ calories.}$$

Time taken to do this = 170 seconds.

Rate of emission of heat =  $\frac{289}{170}$  calories per second.

This is the rate of emission of heat when the mean tem-

perature is  $24.5^{\circ}\text{C}$ ., and *this rate is the same whatever the contents of the drum.*

It is therefore the rate of emission when the drum contains alcohol.

The alcohol took 82.5 seconds to cover the range, and so the total heat given out was—

$$\frac{289}{170} \times 82.5 \text{ calories.}$$

This is therefore the heat given out by the drum and alcohol cooling  $1^{\circ}\text{C}$ .

Now the mass of the alcohol is  $250 \times .83 = 207$  gms. So the heat given out in cooling  $1^{\circ}$  is—

$$207 S + 39 \text{ calories.}$$

$$\text{Thus } 207 S + 39 = 289 \times \frac{82.5}{170} = 289 \times \frac{1}{2.06}$$

In the same way we could compare the values for any of the other temperature ranges, and the expression would be the same except that for 2.06 we should have the ratio of the times for that particular range. In working out the result we take the mean value 2.1 for this ratio, and we have—

$$207 S + 39 = \frac{289}{2.1}$$

$$\text{or } 434.7 S + 81.9 = 289$$

$$S = \frac{207.1}{434.7}$$

$$= .48.$$

If a Callendar apparatus is not available, an arrangement such as that shown in Fig. 46 works well.

A is a tin, the lid of which is fitted with a cork through which pass a thermometer D and a short piece of glass tubing which serves as a bearing for the stirrer B. This is made of wire gauze soldered to a knitting needle, and driven through a flexible coupling C (a spiral spring secured with corks) by a small motor. B rests on a cardboard support F in a larger tin E, which is surrounded by cold water kept constantly circulating and which is supported on metal blocks G.

E has to be weighted to keep it from floating. The top of E is closed by two pieces of cardboard.<sup>1</sup>

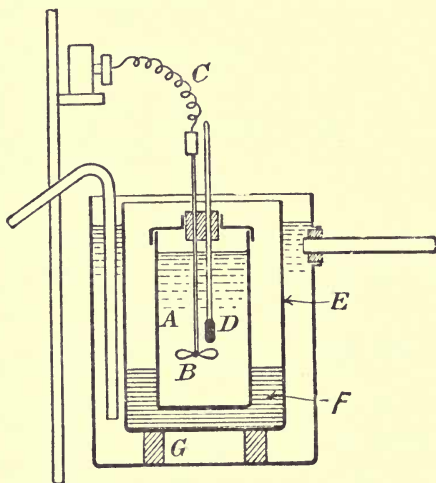


FIG. 46.

### Specific Heat of Gases.

The methods of determining these are discussed in Chapter XIX.

**Variation of Specific Heat with Temperature.**—It is found that in general the specific heat of a solid or liquid is not quite the same at different temperatures. The experiments we have considered have been mostly to determine the mean value over a range between about  $20^{\circ}\text{C.}$  to  $100^{\circ}\text{C.}$  In the case of solids the value at high temperatures is in general greater than at low. Thus for iron the mean specific heat

<sup>1</sup> Any form of apparatus for this method must provide for very adequate stirring and also constancy of the cooling conditions. As regards the latter, conduction and convection account for the greater part of the heat loss (at such temperatures as are likely) and the design of the apparatus must be based on this fact. The rotating Callendar apparatus is particularly satisfactory from this point of view; on the other hand its water equivalent is rather large.

over the range  $20^{\circ}$  to  $100^{\circ}$  C. is about  $\cdot 12$  and the mean specific heat over the range  $0^{\circ}$  to  $1100^{\circ}$  C. is about  $\cdot 15$ .

It should be noted that the specific heat of a substance over any range denotes the ratio of the mean thermal capacity of the substance over that range to the thermal capacity of water at some particular temperature, usually  $15^{\circ}$  C. or  $20^{\circ}$  C. (see page 128). We do not compare it to the thermal capacity of water over the whole range, even if we could have water existing at all the temperatures.

## CHAPTER VIII

### HEAT ENGINES—THE RELATION OF HEAT AND WORK

We have seen that one of the effects of heat on most substances is to cause expansion ; this effect is the basis of what is perhaps the most important practical application, i.e. heat engines. Heat engines are devices for obtaining mechanical work by means of heat, and the term includes hot-air engines, steam engines (including turbines), and internal combustion engines. A detailed consideration of the development of these engines would take up too much space in a book of this size ; at this stage it will be sufficient to consider certain broad principles.

Fig. 47 represents an extremely simple form of a hot-air engine.<sup>1</sup> A flask A, containing air, is connected by a short

<sup>1</sup> This device is due to Principal E. H. Griffiths and was shown by him at a course of lectures given at Leeds in 1900, which the present writer, as a small boy, was privileged to hear ; the lectures are printed in the form of a book, *Thermal Measurement of Energy*, published by the Cambridge University Press.



tube to a U-tube B containing mercury. The short tube has a branch closed by a tap C. On placing a small flame under A the air expands, pushing down the mercury in one limb of B and raising it in the other. C is then opened for a moment and then closed ; this lets out some air and allows the mercury to drop back. The momentum of the mercury causes it to overshoot its equilibrium position and rise some way up the nearer limb ; if the amount in the tube is correctly adjusted the mercury will go on oscillating as long as the flame is applied to A.<sup>1</sup>

The operations which go on are as follows : the air takes

<sup>1</sup> As the successful working of the engine sometimes presents considerable difficulty the following details may be useful as time savers :—

*Setting up the apparatus.* The quantity of mercury has to be adjusted to the dimensions of the flask by trial. The flask should not be too large. The dimensions of the apparatus which I am using at present are :

Diam. of flask, 7 cms.

Length of U-tube (i.e. vertical height from the bottom of the bend to the top of the open limb), 21 cms.

External diameter of the U-tube limbs, 2 cms.

Vertical height from bottom of the bend to the top of the surface of the mercury (when at rest), 14.5 cms.

The U-tube was one which happened to be available and the size of the flask to work with it was found by trial. The flask is Jena glass and is heated by a spirit lamp. The flame must play on the glass surface and with a bunsen burner the engine quickly blows a hole in the flask on the compression stroke.

*Starting.* Even when the adjustments are correct the engine will not always start very easily ; I have found however that the following method can always be relied upon :—The flask is heated by the spirit lamp and as it expands the tap is opened and is kept open until expansion ceases, i.e., until on closing the tap the mercury surfaces remain at the same level. This is important. The tap is then closed and the oscillation started by introducing a glass rod (about 1 cm. thick) into the open end of the U-tube and working it up and down at about the proper period for the mercury for a few times (one can easily tell by the feel whether the vibrations are forced or not). On withdrawing the rod the oscillations should continue ; if they do not the process can be repeated. The engine will go on indefinitely and the amplitude can be adjusted by altering the height of the flame. A range of motion of about 5 cms. is suitable. The period of the engine quoted above is .8 secs.

in heat and expands, pushing the mercury outwards ; it then loses heat to the walls of the tube and neck of the flask and therefore contracts, allowing the mercury to come back. It then takes up more heat and expands again, and so the process continues.<sup>1</sup>

Although this device is merely a pleasing toy and could

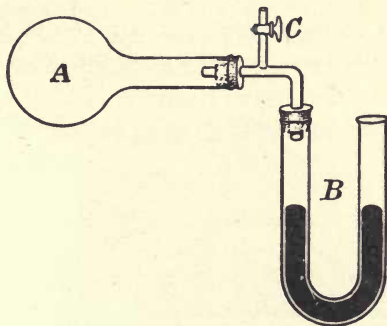


FIG. 47.

not be of any practical use, it has the essentials of a heat engine, i.e. :—

- (1) The working substance (air) which expands if heated.
- (2) A source of heat (the flame) from which the working substance takes in heat to enable it to expand.
- (3) A cooling arrangement so that when the air has performed its working stroke it can give up heat and so contract and get back to its original size ready for the next stroke.

It will be noticed that this third stage is essential in order to get continuous work from the engine. We shall see that in all heat engines this rejection of heat occurs and it is an important point ; there will be a good deal to be said about it later on.

Practical hot-air engines have been constructed using a cylinder and piston in place of the flask and mercury ; they

<sup>1</sup> The mercury has to be adjusted so that its natural period of oscillation in the tube suits the rate of taking in and rejecting heat. The adjustment is often a matter of some difficulty.

have an important addition (the displacer), but they work on this alternate heating and cooling of air. They are not much used in practice (except for such purposes as running small stirring apparatus in a laboratory) because they would have to be very large indeed to develop any considerable power ; a very large volume of air would be needed to get a reasonable expansion.

In the steam engine, advantage is taken of the fact that when water is heated and turned into steam a very large volume

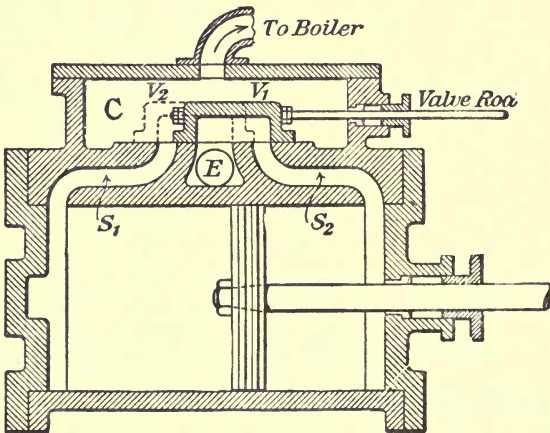


FIG. 48.

change takes place. The volume of steam at  $100^{\circ}\text{C}$ . and atmospheric pressure is about 1,700 times that of the water from which it is formed, and this makes it a much more suitable working substance than air. Fig. 48 represents a section of an ordinary double-acting slide-valve cylinder. Steam from the boiler enters the steam-chest *C* and passes down the passage *S*<sub>1</sub> driving the piston *P* to the right. The slide valve *V* prevents the steam getting into the passage *S*<sub>2</sub>. The slide valve then moves to the position *V*<sub>2</sub> shown by dotted lines, whereby steam passes from the steam-chest

down  $S_2$  urging the piston to the left, while the steam left in the cylinder from the previous stroke passes up  $S$  to  $E$  which is connected to an exhaust pipe leading to the open air (non-condensing engines) or to a condenser. Thus steam is admitted to alternate ends of the cylinder, and after performing its stroke is let out to the air or to the condenser.

Although the arrangement is different from that of the hot-air engine, there are the same fundamental operations as before, i.e. : (1) The working substance (water) takes in heat when it is in the boiler and is turned into steam ; (2) the steam in virtue of its pressure, due to the expansion when water evaporates, performs its working stroke ; (3) the piston is brought back by allowing the steam to pass out carrying a large amount of heat with it which is given up to the air or to the condenser.

The internal combustion engine makes use of the fact that when a mixture of gas and air or petrol vapour and air is ignited, a large amount of heat is generated and the gaseous products of the explosion owing to their high temperatures occupy a large volume. Fig. 49 represents a simplified section of the cylinder of an ordinary four-stroke engine with overhead valves. The mixture of gas or vapour and air comes into the inlet space  $I$ , while  $E$  communicates with the exhaust. There is only one working stroke in every two revolutions, and the process is as follows :—

As the piston  $P$  moves down,<sup>1</sup> the valve 1 is made to open by the valve operating mechanism, and the mixture is drawn into the cylinder. The valve 1 then closes and the piston moves up compressing the charge into the top of the cylinder. As the piston reaches the top the charge is ignited by means of the sparking plug  $S$ , and the force of the explosion drives the piston down ; this is the working stroke. When the piston begins to come up again, the valve 2 is opened allowing the products of combustion to be swept out into the exhaust  $E$ . The operations are then repeated. A heavy flywheel is

<sup>1</sup> If the engine is not already running it has to be started by external agency.

provided so that its momentum will enable the piston to move through its three non-working strokes.

As before we have the same three fundamental operations, i.e. : (1) The working substance is supplied with heat (from the combustion); (2) the working stroke is performed ;

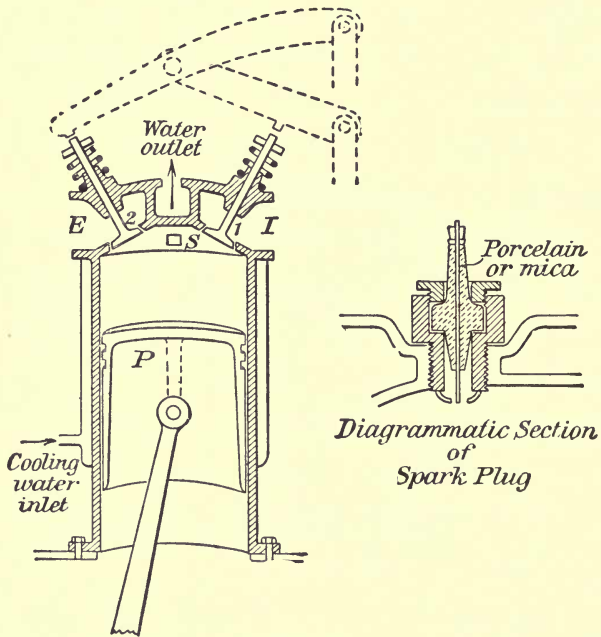


FIG. 49.

(3) the working substance is let out, giving up a large amount of heat to the air.

In these engines the cylinder has to be cooled either by a water-jacket or by air, and a good deal of heat from the explosion is ultimately dissipated in this way also.

**Work done by an Engine. Brake Horse-power.**

*Definition of Work.*—When a force is applied at a point and the point of application moves, work is said to be done, and



the amount of work is given by the product of the force and the distance moved by the point of application, the distance being measured in the direction of the force.

Thus, if we have a 100-lb. weight and we try to lift it and fail, no work has been done, although a force may have been exerted. But if we raise the weight 1 foot, we have done 100 foot-pounds of work; if 2 feet, we have done 200 foot-pounds, and so on. If, however, we push the weight horizontally 2 feet, we have not done 200 foot-pounds; for example, it may need a force of 20 lb. weight just to move the weight against friction, and in this case we shall have done  $2 \times 20 = 40$  foot-pounds of work. It will be observed that there is no question of time; if the 100-lb. weight is raised 2 feet, we have done 200 foot-pounds however long we took over it.

*Power.*—Power is defined as the rate of doing work; in engineering it is usually measured in horse-power. An engine is said to be working at the rate of 1 horse-power if it is doing 33,000 foot-pounds per minute or 550 foot-pounds per second. This number was based on experiments, but, as a matter of fact, it represents rather an exceptional horse.

In measuring the power of an engine we might set it to wind up a weight and so calculate the work done in a given time; this, however, would be most inconvenient as, unless the engine is very small, very large weights or very great heights would be involved. It is more convenient to set the engine to work against the friction of some sort of brake; the work done can then be measured as described below.

Fig. 50 represents a rope passing over the rim of a wheel on the engine shaft. A weight  $W$  is suspended at one end of the rope and a spring balance is attached to the other. If the wheel is rotating as shown, the friction of the rope on the wheel will have a tendency to raise the weight; the difference between the weight and the reading of the spring balance will give the frictional force, since the frictional force and the spring balance between them support the weight.

Thus, suppose that the weight were 20 lb. and the spring

balance read 7 lb. Then  $20 - 7 = 13$  lb. wt. represents the frictional force.

Now consider the portion AB of the rope which is in contact with the wheel. If this isolated portion were pressed against the wheel so that the frictional force remained the same, i.e. 13 lb. wt., and the wheel were at rest, the work done if the piece were hauled once round the wheel by means of the end A would be 13 lb.  $\times$  distance A moves, i.e.  $13 \times$

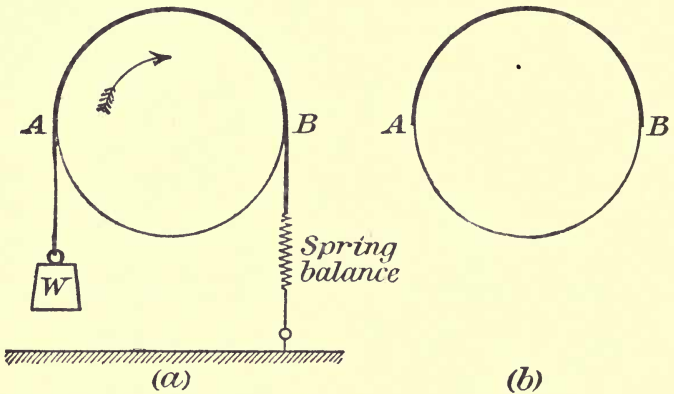


FIG. 50.

circumference of the wheel (strictly the circumference of the circle formed by the central line of the rope).

The same work is done if AB remains at rest and the wheel turns one revolution; hence in our actual case the work done against friction per revolution is  $13 \times$  circumference of wheel (neglecting thickness of rope). So that in order to find the work done per minute, all we have to do is to read the spring balance and find by a revolution counter (or a tachometer) the number of revolutions per minute. Then work done per minute =  $(W - \text{spring balance reading}) \times$  circumference of wheel in feet  $\times$  number of revolutions per minute. This value divided by 33,000 gives the horse-power.

Horse-power measured in this way is known as brake

horse-power (B.H.P.), and represents the net power the engine develops <sup>1</sup> irrespective of any frictional or other losses in the engine itself.

**The Relation between Heat and Work.**—We have seen that a heat engine takes in a certain amount of heat and that some heat is rejected; the amount rejected is found to be less than that taken in, so that when all the heat is accounted for some heat disappears in the process. The amount which disappears increases as the work done by the engine increases. Thus in a heat engine heat disappears and work is obtained. On the other hand, as we saw in Chapter I, when work is done against friction heat is produced. So that heat can be obtained from work and work from heat. Moreover it has been established by the experiments of Joule (begun in 1840 and extended over many years) and others that there is a definite rate of exchange; if a certain amount of work is used up a definite amount of heat is produced and vice versa. The amount of work required to produce a unit of heat is spoken of as the *Mechanical Equivalent* of heat (denoted by  $J$ ); this is also the amount of work which is produced when one unit of heat is completely used up in producing work.

**Determination of the Mechanical Equivalent.**—When work is done against friction, heat is produced as described in Chapter I. Thus, in determining the brake horse-power of an engine the brake and the wheel become heated.<sup>2</sup> If we can measure the total amount of heat produced at the same time as the work done is determined we can at once obtain the mechanical equivalent. This is the basis of a very convenient laboratory method due to Callendar.

The general idea is to have a hollow brass drum mounted on a shaft. Around the drum passes a silk belt, with a weight

<sup>1</sup> The brake should be adjusted so that the engine runs at its normal speed; in practice it is usual to have a second spring balance in place of the weight and some means of tightening the belt until the friction is a suitable amount.

<sup>2</sup> For this reason the method cannot be adopted for engines of large power, since the amount of heat developed is unmanageable, and other methods of determining B.H.P. have to be used.

suspended at one end and a spring balance at the other. The number of revolutions of the shaft can be read off on a cyclo-meter geared to it. Thus the work done can be determined from the number of revolutions, the circumference of the drum, and the difference between the forces at the two ends

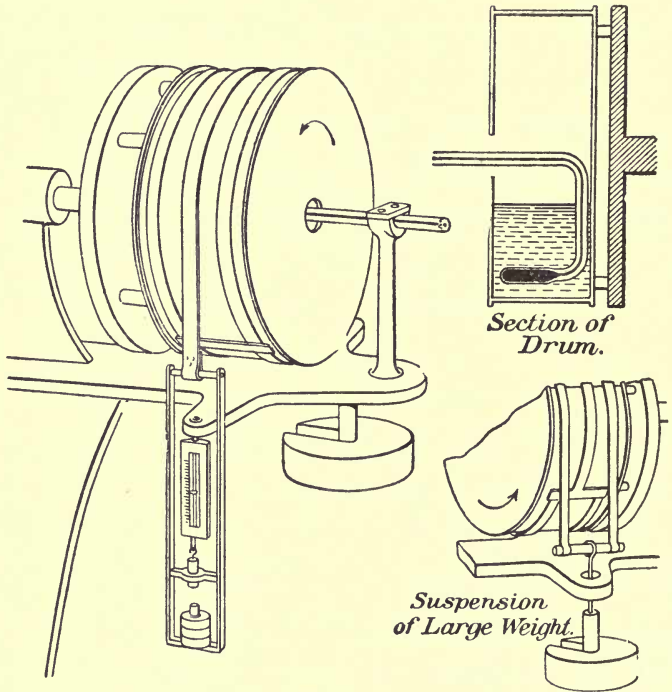


FIG. 51.

of the belt. A known weight of water is placed in the drum, and a thermometer bent into the shape shown in Fig. 51 enables the temperature to be determined. Thus as the drum is heated by friction the water is heated also, and the amount of heat developed is obtained from the weight of water, the water equivalent of the drum and the rise in temperature. Since the drum rotates while the water does not, every part

of the drum (except the part just near the axis) is constantly being brought in contact with the water. Thus we can measure the work done against friction and the heat produced by the friction, and so we have the amount of heat produced by this amount of work.

The apparatus is capable of giving extraordinarily consistent and accurate results, but in order that this may be accomplished care is necessary in the measurement of the heat developed, and the cooling correction (page 96) becomes important. The writer has modified the procedure recommended by the makers, and, as a number of interesting points arise, the operations are described in some detail.

Fig. 51 shows the general arrangement. The silk belt passes  $1\frac{1}{2}$  times round the drum and is provided at each end with a short brass bar. To one of these is hooked a fairly heavy weight, while the other is not attached to the spring balance but a frame of known weight (to which other small known weights can be added) is hooked <sup>1</sup> on to it; the spring balance helps to support this frame. Thus the force on the end of the belt is given by weight of frame and small weights—spring balance reading. There is also attached to this end of the belt a short piece of elastic provided with a hook; this hangs freely during the first part of the operation but is used in the cooling correction.

The drum is driven, through reduction gearing, by an electric motor, which should be provided with a controlling resistance; a suitable speed for the drum is about 120 r.p.m.

Two hundred and fifty gms. of water are put into the drum by means of a pipette; care should be taken not to get any water on the outside. It is desirable to start with the water at about atmospheric temperature. The motor is started and the speed suitably regulated; the large weight should "float" between its stops.<sup>2</sup> At each minute readings of the

<sup>1</sup> As supplied by the maker, the frame is screwed to the bar.

<sup>2</sup> A preliminary adjustment is made by altering the point of attachment of the spring balance to the frame; further adjustment can be made while running (if necessary) by adding or taking away one or more of the small weights, but see note, page 118.



temperature, revolution counter and spring balance are taken : after about eight or ten minutes the motor is stopped, readings are taken, the heavy weight and the frame are unhooked from the ends of the belt. The two ends are then connected by the piece of elastic with the hook so that the belt continues to encircle the drum but now will revolve with it freely, the motor is started up again and the speed adjusted until it is about the same as before. All this takes about half a minute. The temperature is then read every minute with the drum still revolving, but no work being done by the belt. This gives the rate of cooling with the conditions as nearly as practicable what they were during the heating ; the operation is continued for six or seven minutes to make sure that regular cooling has set in.

The figures on p. 115 taken from an experiment will be used to illustrate the method. Columns 1, 2, 5 and 6 give the observed readings ; 3 and 4 are calculated as explained later.

During the heating, the friction takes place at the *outside* of the drum. As the drum is a good conductor and its surface is constantly in contact with the water, most of the heat developed goes to raise the temperature of the drum and its contents and not much passes outwards through the silk ; the mass of the latter is also very small compared with that of the drum and contents. The temperature of the drum must be slightly above that of the water, and when the motor stops the temperature indicated by the thermometer does not immediately fall, as some of the heat developed has not had time to pass to the water.

**Measurement of the Heat. Cooling Correction.**—As soon as the drum and its contents are at a higher temperature than the surroundings, they begin to lose heat by conduction, convection and radiation. This heat is supplied by the work done and must be added to that determined by the rise in temperature. If the temperature of a hot object is only a few degrees above that of its surroundings it is fairly near the truth to assume that the rate of loss of heat is propor-

Room temperature 13° C.

Time (mins.)	Temp. ° C.	Mean Temp. during the Interval.	Rate of fall of Temp. from Graph.	Revn. Counter.	Spring Balance (lb. wt.)
0	13.4	14.4	.05	12,087	Immediately after starting.
1	15.4				.55
2	17.3	16.35	.15	12,217	.55
3	19.2	18.25	.25	12,347	.55
4	20.9	20.05	.3	12,483	.55
5	22.6	21.75	.4	12,620	.5
6	24.2	23.4	.45	12,753	.5
7	25.8	25.0	.55	12,888	.45
8	27.2	26.5	.6	13,026	.45
	Motor stopped.	Weights unhooked.	2.75 Motor started.	13,161	
8½	27.2	about 27.1	.65		
9	26.8	Fall per minute.	3.40		
10	26.2	.6°			
11	25.6	.6			
12	25.1	.5			
13	24.6	.5			
14	24.1	.5			
15	23.7	.4			
16	23.3	.4			

Load at one end of belt = 4,275 gms. wt.

Load at other end of belt = (473 gms. wt. - spring balance).

Mass of drum = 421 gms.

Specific Heat of brass = .092.

w.e. of drum =  $421 \times .092 = 39$  gms. wt.

tional to the difference in temperature between the object and its surroundings. This law, known as Newton's Law of cooling, does not hold for large differences of temperature (see page 237), but may be regarded as sufficiently accurate for such cases as the present. To determine its amount we take the observations after the cooling conditions have settled down.<sup>1</sup> From the 9th to the 11th minute the rate of fall of temperature is  $\cdot 6^{\circ}$  C. per minute; the mean temperature during this interval is  $26\cdot 2^{\circ}$  C. Plot a graph in which abscissae represent mean temperatures of the water, and ordinates the rate of fall of temperature in degrees per minute.

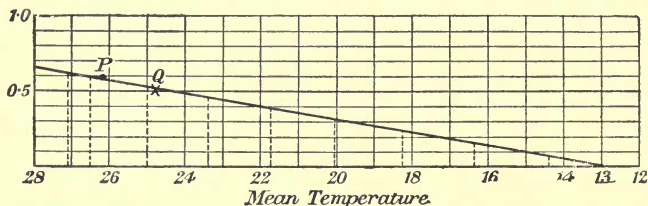


FIG. 52.

The point P represents the rate  $\cdot 6^{\circ}$  per minute for a mean temperature  $26\cdot 2^{\circ}$  C. Join this point by a straight line to  $13^{\circ}$  C., the room temperature. This straight line gives us the rate of fall of temperature corresponding to any given mean temperature. (As a check, Q represents the rate,  $\cdot 5^{\circ}$  C. per minute corresponding to  $24\cdot 8^{\circ}$ , got from the readings from the 11th to the 14th minute.)

From this graph we get the rate of cooling corresponding to the mean temperatures shown in column 3 of the table. These values are shown in column 4. During the first eight minutes, the total loss of heat is that given out by the drum

<sup>1</sup> When the temperature is falling, the drum must be slightly cooler than the water; it is assumed that this condition has set in after the 9th minute, since the rate of cooling is gradually diminishing. From the 8th to the 9th minute the fall of temperature is less than that which is observed later, when the mean temperature is lower; this must mean that the fall in temperature of the water does not indicate the whole of the heat loss.

and contents falling through the sum of all the separate amounts, i.e.  $2.75^{\circ}$ ; during the 9th the loss of heat is that corresponding to a fall of  $.65^{\circ}$  C. If none of this heat had been lost the temperature at the end of the 9th minute would have been  $26.8 + .65 + 2.75 = 30.2^{\circ}$  C.<sup>1</sup> Thus, if no loss had occurred, the final temperature of the water would have been  $30.2^{\circ}$  C.

We can now calculate the value of J.

To get the heat produced we have 250 gms. of water + the drum were heated from  $13.4^{\circ}$  C. to  $30.2^{\circ}$  C. Taking the water equivalent of the drum as 39 gms., this corresponds to 289 gms. of water or  $\frac{289}{454}$  lb. of water.

$$\text{Heat produced therefore} = \frac{289}{454} \times 16.8 \text{ T.U.}$$

To get the work done—

Load on one end of belt	=	4,275 gms. wt.
Load on other end	=	(473 — mean spring balance reading)
	=	(473 — $.51 \times 454$ )
	=	242 gms. wt.
Force of friction	=	4,275 — 242 = 4,033 gms. wt.
	=	$\frac{4,033}{454}$ lb. wt.
Diameter of drum	=	6 inches = .5 feet.
Work done per revolution	=	$\frac{4,033}{454} \times \pi \times .5$ foot-pounds
Total revolutions	=	13,161 — 12,087 = 1,074.
Total work done	=	$\frac{4,033 \times \pi \times .5 \times 1,074}{454}$ foot-pounds
		produce $\frac{289}{454} \times 16.8$ T.U.
$J = \frac{4,033 \times \pi \times .5 \times 1,074}{289 \times 16.8}$		foot-pounds per T.U.
		= 1,401 foot-pounds per T.U.

<sup>1</sup> Observe that during the 9th minute the fall in temperature recorded is less than that corresponding to the mean temperature, which means that some of the heat generated by friction is still coming in. After the 9th minute, if we add on the cooling correction the temperature would remain constant since no more heat is coming in.

**Note on the Above Experiment.**—It is sometimes pointed out that the cooling correction can be avoided for practical purposes by starting with the water at a temperature below that of the room and stopping when the temperature is about the same amount above that of the room. This arrangement limits the range of temperature, since if the water starts at more than  $3^{\circ}$  or  $4^{\circ}$  below room temperature one is apt to get a deposit of dew on the drum, in which case the friction is very irregular. The writer prefers to obtain a larger range and apply a cooling correction. But the cooling correction is very unreliable if the drum is at rest during the observations; the water should be continually brought into contact with all parts of the drum, if the readings of the thermometer are to be taken as representing the mean temperature of the drum and its contents. Emission of heat takes place from all parts of the drum, and if the water remains in one place and is not stirred the temperature will vary at different parts. With the drum rotating, the writer finds that the cooling is very regular; with the drum at rest it is very irregular. Even as it is, the drum being hotter than the water during heating, the loss of heat must be somewhat greater than that deduced from the cooling curve; the design of the apparatus is such that this difference is small. The tendency is therefore for  $J$  to come out rather above than below the accepted value. One other point may be noticed. The instrument is usually supplied with a spring balance reading in grammes; the writer substitutes a rather stiffer one reading to  $\frac{1}{10}$  lb. By this means the minor variations in the friction are much less troublesome; no adjustment is necessary during the running. With the more sensitive spring greater care is necessary in attending to the polish of the friction surface than is convenient in an ordinary laboratory. One-tenth lb. is only about 1 per cent. of 4,275 gms., so that the measurement of the work is quite as accurate as the determination of temperature is likely to be; for the same reason it is legitimate to take a mean value for the spring balance reading as described, instead



of getting the separate values of the work done in each minute. By adopting the procedure described, the writer finds that without any trouble or previous preparation the result obtained can be trusted to be within about 2 per cent. of the accepted value, i.e. somewhere between 1,400 and 1,430 foot-pounds per T.U., and although the apparatus may be capable of greater accuracy, comparatively few people are likely to get the temperature measurement better than within 2 per cent. without more elaborate precautions.

**The Thermal Efficiency of an Engine.**—Since a unit of heat is equivalent to a definite amount of work, and we can find the calorific value of any kind of fuel, we are able to calculate the amount of work which should be produced by burning a known weight of fuel if all the heat were converted to work. Thus, if we know the work which an engine can do in a given time (as determined by the B.H.P.) and the amount of fuel it uses in that time, we can find out whether the engine is wasteful or not.

The thermal efficiency of an engine is defined as—

$$\frac{\text{Work done by the engine in a given time}}{\text{Work equivalent to the heat value of the fuel used in that time.}}$$

To take an example. A good steam engine of large size is found to take about 1.3 lb. of coal per hour for each horse-power developed. Taking the calorific value of coal as about 8,000 T.U. per lb. we have—

$$1.3 \text{ lb. of coal give } 1.3 \times 8,000 \text{ T.U.} = 10,400 \text{ T.U.}$$

But since 1 T.U. corresponds to 1,400 foot-pounds, 10,400 T.U. corresponds to  $10,400 \times 1,400 = 14,560,000$  foot-pounds. But the work actually got from this is 1 horse-power for 1 hour

$$= 33,000 \times 60 = 1,980,000 \text{ foot-pounds.}$$

$$\begin{aligned} \text{Thermal efficiency} &= \frac{\text{Work actually done}}{\text{Work ideally possible}} \\ &= \frac{1,980,000}{14,560,000} = .13 \text{ or } 13 \text{ per cent.} \end{aligned}$$

In practice the thermal efficiency of heat engines is low ; 13 per cent. is not a bad value for large steam engines.

Internal combustion engines may have a higher value under certain conditions ; some Diesel engines have reached 38 per cent., while the Stirling engine (a combined steam and explosion engine) is claimed to have given 42 per cent.

This low efficiency is to some extent due to mechanical imperfections, but more to the fact which we have already noticed that heat engines do not make use of all the heat taken in, but return a large amount to the atmosphere or condenser and this heat is of no use to the engineer. As we shall see in Chapter XXI, there is no hope of avoiding some rejection of heat, so that no improvement of design is likely to bring the efficiency of any heat engine anywhere near 100 per cent.

**The Nature of Heat. Development of Modern Ideas.**—Down to about the end of the eighteenth century, the prevailing ideas about the nature of heat were summed up in the caloric theory ; according to this theory heat was a kind of invisible fluid<sup>1</sup> called “caloric” which filled the spaces between the particles of matter. On this theory, the fact that percussion or compression gave rise to “sensible heat” was accounted for readily enough ; the caloric was supposed to be squeezed out, like water out of a sponge. It was not quite so easy to account for the production of heat by friction, but it was considered that the small particles of the material which were rubbed off had a smaller capacity for heat than the original solid, and so some of the caloric made its appearance. There seems to have been no attempt to determine by experiment whether the capacity for heat of the small particles was really less than that of the solid.

In 1798, however, experiments were made by Benjamin Thomson, Count Rumford. He had been struck by the very great development of heat during the boring of brass cannon in which he was engaged at Munich. He carried out experiments on a small hollow cylinder of gun metal, some 10 inches long and

<sup>1</sup> It was generally regarded as being imponderable, but as late as 1785 a paper is to be found in the *Phil. Trans.* in which the author describes experiments undertaken to find out whether it was possible to detect any change in weight of a body to which caloric is supplied and he concluded that he had detected a change.

8 inches diameter. He used a blunt borer, as he wanted to see whether less heat would be developed in consequence of the conversion of a smaller amount of material into metallic chips and dust. He found that a very large amount of heat was developed, in spite of the fact that the amount of metal removed was very small. Furthermore, in order to see if the exclusion of the atmosphere had any effect, he placed the cylinder in a box filled with water; after a time ( $21\frac{1}{2}$  hours) the water boiled. There was therefore no question of heat being abstracted from the atmosphere.

He pointed out that a very large amount of heat was given off continuously in all directions; it was difficult to imagine that this could come as the result merely of a change in the capacity for heat of the insignificant amount of material removed. Moreover he showed by experiment that the capacity for heat of the metallic chips was practically the same as that of the solid. He lays great stress on the fact that the supply of heat is apparently inexhaustible; as long as the borer is worked there is no sign of any exhaustion. He concludes: "It is hardly necessary to add that anything which any *insulated* body or system of bodies can continue to furnish without *limitation* cannot possibly be a *material substance*; and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in the manner the heat was excited and communicated in these experiments except it be MOTION."<sup>1</sup>

Experiments performed by Humphry Davy were however even more strikingly at variance with the caloric theory. Davy arranged that two pieces of ice should be rubbed together, and in the later experiments this was done by clockwork, the whole apparatus being under the receiver of an air pump. The ice was found to be melted at the surface where the rubbing took place and not elsewhere. Now in order to turn ice to water, heat is required (see Chapter IX), while the capacity for heat of water is greater than that of ice. The heat, therefore, could not have come out of the ice, as the result of its change to water.

It is difficult to conceive of any single experiment which is more contrary to the reasoning of the calorists, but the fact remains that they were not convinced, and even Davy himself

<sup>1</sup> Rumford, *Phil. Trans.*, 1798.

appears afterwards to have had doubts of which he did not rid himself for some time.

The experiments of Davy and of Rumford mark the beginning of the modern idea of heat, but the real foundation was laid by the experiments of Dr. Joule of Manchester, begun in 1840 and continued for many years. Rumford's account of his experiment makes it fairly clear that he had a general idea that the amount of heat depended on the work done, but Joule set out to determine the matter with accuracy; he arranged experiments in which the work done and the heat produced were measured. In one set of experiments water was churned by a revolving paddle; the paddle was driven by means of weights which descended a known distance.

Fig. 53 shows a rough idea of the arrangement. W, W are two

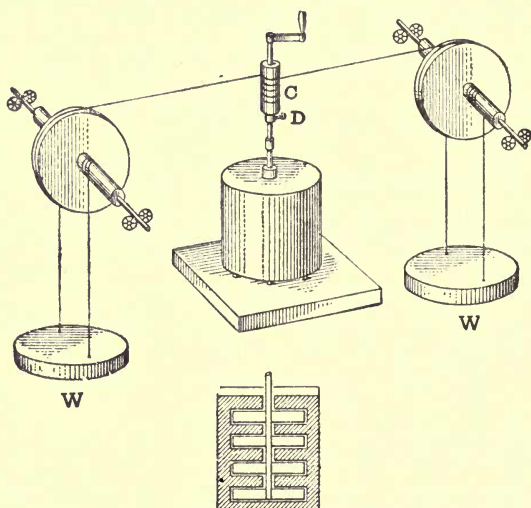


FIG. 53.

weights, which by their descent cause the vertical shaft C to rotate and drive the paddle in the calorimeter which contains a known weight of water. In order that the water might not be



merely carried round with the paddle and so give rise to very little friction, the inside of the calorimeter was provided with fixed partitions with openings through which passed the arms of the paddle, as shown in the section in Fig. 53. When the weights reached the ground the paddle shaft was disconnected from the roller by the screw D (Fig. 53) and the weights quickly wound up again. The shaft was connected again and the weights released. In this way some twenty descents of the weights were carried out, while the rise in temperature of the water was determined by a thermometer.

The work done was determined by the total distance the weights descended, a correction being applied for the friction of the bearings and for the fact that the weights reached the ground with a certain speed and so possessed kinetic energy.

The heat produced was determined from the mass of water + water equivalent of calorimeter and paddles and the rise in temperature. Corrections were applied for loss of heat to the surroundings.

Joule carried out experiments in which the heat was generated in other ways; he used liquids other than water and also the friction between solids, compression of air, etc. In all these experiments he found that the amount of work required to produce a unit of heat came out as about the same; he regarded the method of churning water as most reliable, and devoted a great deal of time to that method. Joule gave as the value for the Mechanical Equivalent 772 foot-pounds<sup>1</sup> for one B.Th.U., i.e. the amount of heat necessary to raise the temperature of 1 lb. of water 1° F. The temperature was measured by a mercury in glass thermometer and was not reduced to the air scale. When this correction is applied to Joule's results, the value comes out as about 778 foot-pounds per B.Th.U.

About 1857 Hirn carried out experiments with a steam engine in which he measured the heat taken in from the boiler and the heat given out to the condenser. After allowing for heat lost in the cylinder by conduction and radiation he found that heat had disappeared, and the amount which disappeared was very much greater when the engine was driving machinery than when it was running light. Deducting the heat returned to the condenser and the heat lost by radiation and conduction from that taken into

<sup>1</sup> Taking the weight of 1 lb. in the latitude of Manchester.



the cylinder from the boiler the amount of heat used up in doing work was determined, and thus a value for the mechanical equivalent was obtained. The result obtained by Hirn in this way was in very fair agreement with that obtained by Joule and others for the inverse operation. The difficulties of the experiment were great, and a very accurate result was not to be expected; it is however of importance as a direct determination of the amount of work produced by a unit of heat.

These experiments are the foundation of the modern view that heat is a form of energy. This is merely a particular case of a more general Principle, known as the Principle of the Conservation of Energy. This Principle states that energy cannot be created or destroyed, it can merely be changed from one form to another. Energy, the capacity to do work, can exist in many forms, thus a weight at the top of a cliff possesses energy due to its position, for it can do work by being allowed to descend. A projectile possesses energy due to its speed, for it can do work in the course of being brought to rest. Energy may exist as electrical energy or in other forms. Coal possesses chemical energy; if burnt it gives out heat. Thus we might burn coal in the furnace of a steam engine and obtain mechanical work; the engine might drive a dynamo giving electrical energy, and this might be used to drive a motor.

In all these cases there is no loss of energy, only a change of form. It is true that a five horse-power engine would not drive a dynamo capable of giving enough energy to drive a five horse-power motor; but in this case all the missing energy can be accounted for in the form of heat developed by friction and in other ways. The Principle of the Conservation of Energy then states that the total amount of energy in an isolated system is constant.

The whole of modern physical science is built upon this Principle, and no experimental result has been found contrary to it; predictions based on it are found to be true.

It is of great importance in Physical Science that the value of the Mechanical Equivalent should be known with accuracy, and many experiments have been made to determine it. A complete account of these experiments would take up far too much space; we may summarize them as follows:—

**Direct methods**, in which water is churned, the mechanical work and the heat produced being measured. In all of these the

method of driving the paddle by descending weights is abandoned, and the work done is measured by some form of friction balance. This method is originally due to Hirn. It may be illustrated by a brief description of Joule's apparatus in his second set of experiments as shown in Fig. 54.

The paddle was mounted on a vertical shaft A as before, but it was driven by hand wheels instead of weights. The calorimeter C did not stand on a fixed support, but was suspended on a bearing so that it could rotate freely about A. When the paddle

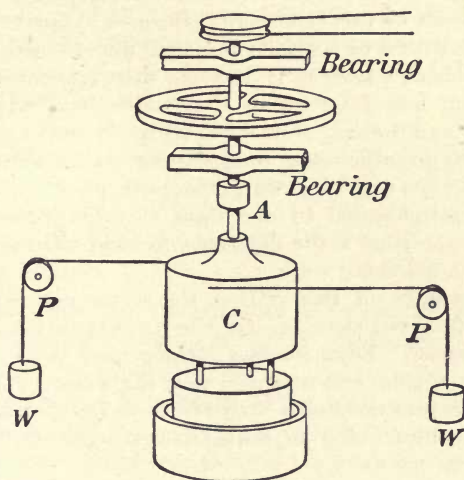


FIG. 54.

was revolving the calorimeter tended to rotate with it. A couple tending to prevent rotation was applied to the calorimeter by two cords which left the calorimeter at opposite ends of a diameter and passed over two pulleys P, P; to the ends of these cords equal weights W, W were attached. The paddle was driven at such a speed that the weights were raised from the floor and kept suspended in one position. Thus the couple due to friction in the calorimeter just balanced that due to the weights.

If  $r$  is the radius of the calorimeter where the cords were attached, this couple is  $2rW$  when  $W$  includes the scale pan.

The work done against friction when the paddle is turned

through an angle  $\theta$  is therefore  $2rW\theta$ ; and in  $n$  revolutions it would be  $2\pi n \times 2rW = 4\pi nrW$ .

The number of revolutions of the shaft was determined by a revolution counter geared to it.

The point of this arrangement is that the work done in the calorimeter is measured, and so no corrections due to friction of driving cords and bearings come in; there are also other advantages. The calorimeter was supported on a hydraulic support which did not hinder rotation and avoided trouble due to the weight of the calorimeter on the bearing and any want of centring.

Experiments of this type were performed by Joule <sup>1</sup> and Rowland,<sup>2</sup> while others of a similar principle were those of Micelescu <sup>3</sup> and Reynolds and Moorby <sup>4</sup>; in these latter experiments the heat measurement was different, in that water flowed through the calorimeter and the rate of flow was adjusted until a steady state was reached in which the temperature of the outflowing and inflowing water was constant; the heat produced in a given time is thus measured by the mass of water which has gone through in the time  $\times$  the difference in temperature of the outflowing and inflowing water.

The advantage of this is that the water equivalent of the apparatus does not come in, and the corrections for loss of heat are much easier. Reynolds and Moorby used large powers (100 H.P. steam engine) and arranged that the water should come in at a temperature not much above  $0^\circ$  C. and come out nearly at  $100^\circ$  C., the idea being to avoid uncertainties of the scale of temperature.

**Electrical Methods.**—Of the indirect methods of determining  $J$ , the electrical are the most important. The general principle is to send a known current through a wire of fairly high resistance immersed in liquid in some form of calorimeter, so as to measure the heat produced in a given time. If  $C$  is the current in ampères and  $E$  the difference of potential in volts between the ends of the resistance, we have from the definition of the electrical units that work is being done at the rate of  $EC$  joules <sup>5</sup> per second.

<sup>1</sup> *Phil. Trans.*, 1878.

<sup>2</sup> *Proc. Amer. Acad. Arts and Sciences*, 1879–80

<sup>3</sup> *Ann. de Chimie et Physique*, 1892.

<sup>4</sup> *Phil. Trans.*, 1897.

<sup>5</sup> 1 joule =  $10^7$  ergs.

The heat produced in a given time is measured in the usual way. Experiments of this type were performed by Schuster and Gannon<sup>1</sup> and by Griffiths<sup>2</sup>; while Callendar and Barnes<sup>3</sup> performed a series of experiments in which the heat was measured by having a flow of water through the apparatus and arranging that a steady state should be attained as in the experiments of Miclescu and Reynolds and Moorby. A steady current of liquid flowed down a narrow tube, along the axis of which is a wire carrying a current  $C$ . A pair of differential platinum thermometers,  $P_1$ ,  $P_2$ , gave the difference in temperature of the inflowing and outflowing water. The potential difference at the ends of the conductor was measured on a potentiometer in terms of a

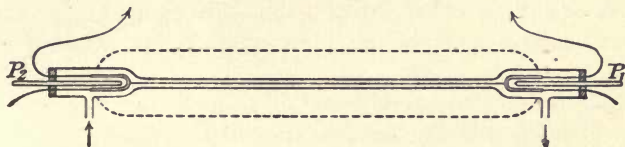


FIG. 55.

standard cell, and the current was measured by including a known standard resistance in the circuit and measuring the P.D. at its ends on the potentiometer.

**Variation of the Specific Heat of Water.**—As soon as accurate methods of measuring  $J$  were available it was seen that the amount of work required to raise the temperature of a given weight of water through  $1^\circ$  depended on the part of the scale of temperature at which the  $1^\circ$  was taken. Before this time experiments of the ordinary method of mixture type had shown variations, but the results were uncertain; the mechanical equivalent method is much more reliable. The most trustworthy results are those of Dr. Barnes with the apparatus described in the last paragraph. His results show that the Specific Heat of water is a minimum at about  $37.5^\circ \text{C}$ .

**The Unit of Heat.**—A calory is defined as the amount of heat required to raise the temperature of 1 gm. of water  $1^\circ \text{C}$ . It

<sup>1</sup> *Phil Trans.*, 1895.

<sup>2</sup> *Phil Trans.*, 1893.

<sup>3</sup> *Phil. Trans.*, 1902.



is evident that this definition has no strict meaning unless we specify at what part of the scale the  $1^{\circ}$  C. is to be taken.

The following units are recognized :—

The  $15^{\circ}$  calory = heat required to raise temperature of 1 gm.  
of water from  $14.5^{\circ}$  to  $15.5^{\circ}$ .

$20^{\circ}$  calory =  $19.5^{\circ}$  to  $20.5^{\circ}$ .

The mean cal. =  $\frac{1}{100}$  of heat required to raise 1 gm. of water from  $0^{\circ}$  to  $100^{\circ}$  C.

The mean and  $15^{\circ}$  calory are very nearly equal and equivalent to 4.184 joules; the  $20^{\circ}$  is about 1 in 1,000 less and equivalent to 4.180 joules.



## CHAPTER IX

### CHANGE OF STATE—SOLID TO LIQUID

If we take a solid substance and heat it, in general the temperature rises and a certain amount of expansion may take place. If we go on, a stage is reached when the solid begins to melt and turn to a liquid.<sup>1</sup> At this stage certain important effects occur.

In the first place it is found that, in general, there is a very perceptible change in volume. In the majority of cases the liquid occupies a larger volume than the solid. This may be illustrated in quite a striking way by melting some paraffin wax in a large test tube and then allowing it to cool. The outside cools first and the result is that when the whole mass is solid, the surface instead of being flat has a deep hollow in it, and there may even be a distinct cavity in the centre. It may be noticed that when pieces of the solid are dropped into the molten wax the pieces sink, indicating that the solid has a greater density than the liquid.

In the case of a few substances, of which water is a striking example, the effect is in the opposite direction; when water turns to ice the volume of the ice is decidedly greater than that of the water. Roughly speaking, 11 c.c. of water form about 12 c.c. of ice. This increase in volume may be shown in the following simple manner (Fig. 56).

A large test tube is half filled with water; paraffin oil or

<sup>1</sup> This is the normal course: exceptions are furnished by substances which decompose before they reach the melting point, and a few substances turn to vapour without passing through the liquid phase, and the vapour if cooled passes back direct to the solid state. Arsenic is an example.

turpentine is poured in on the water until the tube is full. The tube is then closed by a cork through which passes a length of quill tubing open at each end ; care must be taken to see that there are no bubbles of air under the cork, and the oil should rise a little way up the quill tube. The test tube is then placed in a freezing mixture of ice and salt. Nothing much appears to happen for a little while, although the oil may sink slightly ; but after a time the oil begins to rise quite quickly and ultimately may flow out of the upper end of the quill tube. If the test tube is now taken out of the freezing mixture the water will be seen to be wholly or partially turned to ice. The paraffin oil or turpentine does not solidify at the temperature of the freezing mixture.



FIG. 56.

A more striking illustration is to take a small, thick-walled cast-iron bottle, fitted with a screw stopper. The bottle is completely filled with water and its stopper screwed home. It is then completely immersed in a freezing mixture of ice and salt contained in a metal dish ; a duster should be placed over the dish. After some considerable time the bottle will burst with a loud crack ; it usually splits cleanly, but the writer has known a large piece to be driven up to the ceiling, and therefore recommends the duster.

In winter this behaviour is sometimes emulated by the water-pipes of a house, to the discomfiture of the occupants. The water in the pipes freezes and splits the pipe by its expansion ; the effect is not usually noticed at the time, but as soon as the thaw comes the water escaping from the rent draws attention to the phenomenon. This trouble is much less likely to happen if the pipes are elliptical in section, since the area of an ellipse is less than that of a circle of the same perimeter and so there is the possibility of some expansion.

The action of frosts in breaking up and loosening the soil—an important effect from the point of view of agriculture—

is another example of this property of water. The water which has percolated into the soil expands when it freezes and the result is that the soil is much broken up; this is very evident as soon as the thaw comes. The weathering of rocks at high altitudes is also largely due to this action; water percolating into cracks by day freezes at night, splitting off pieces of the rock. In many cases the ice holds the piece in position until the sun gets up and melts the ice, when falls of rock occur; on the other hand, big masses too large to be bound by the ice are split off and fall at night; and Mr. Whympfer noticed that on each of seven nights which he spent on the south-west ridge of the Matterhorn the greatest rock falls occurred in the night between midnight and dawn, this period being the coldest part of the twenty-four hours.

**The Latent Heat of Fusion.**—Another phenomenon connected with change of state is that when a solid turns to a liquid heat must be absorbed by it. This may be illustrated by the experiment shown in Fig. 57.

A vessel of thin copper is supported from the ring of a retort stand. A stirring gear, consisting of a vertical shaft with a piece of wire gauze soldered to it and bent in the shape of a propeller is provided; the propeller must be near the bottom of the vessel. A thermometer is placed in the position shown. The vessel is filled with small pieces of ice, care being taken to put in as much as possible. The temperature is noted, and the apparatus is lifted by the stand and placed so that the copper vessel is in the steam from a large beaker of boiling water. The thermometer is read every half-minute. A small motor is connected to the stirrer by a string belt. At first the stirrer cannot turn, but when a fair amount of ice is melted, the remainder floats and the propeller can turn in the water at the bottom.

Readings of the temperature are continued until all the ice is melted, and for some time after; as long as any ice is present it can be heard rattling against the vessel and thermometer, and so it is easy to tell when it has all gone. The

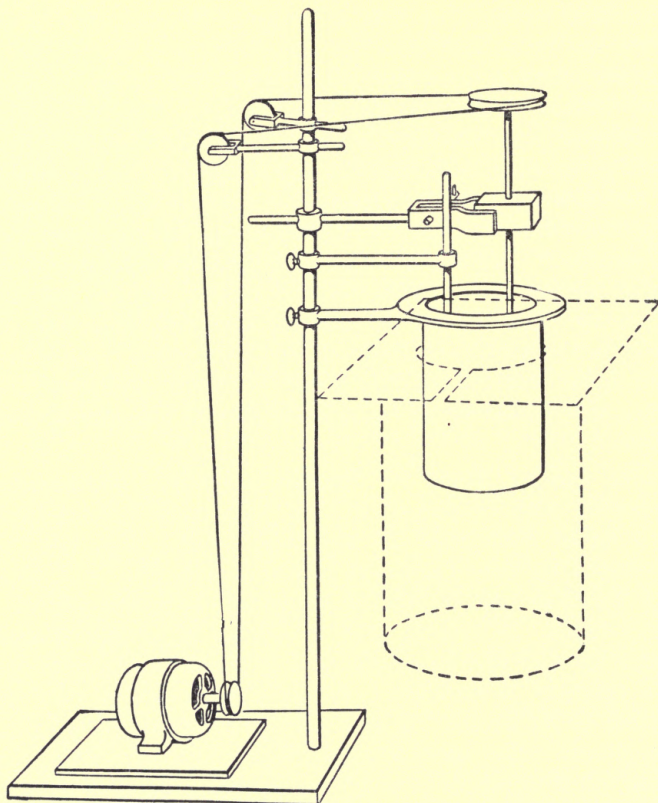


FIG. 57.

readings (p. 133) obtained in an experiment illustrate what happens.

The ice had all melted just after the 8th minute. The propeller started at the 4th minute. The results are plotted on the graph shown in Fig. 58.

Now the vessel was receiving heat from the steam all the time, but until the ice has all been melted the temperature hardly rises appreciably; it does not do so at all while there



Time.	Temp.	Time.	Temp.	Time.	Temp.
mins.	°C	mins.	°C	mins.	°C
0	0	4	0	8	3.5
$\frac{1}{2}$	0	$4\frac{1}{2}$	.5	$8\frac{1}{2}$	7.5
1	0	5	1.0	9	12
$1\frac{1}{2}$	0	$5\frac{1}{2}$	.5	$9\frac{1}{2}$	17
2	0	6	.5	10	22
$2\frac{1}{2}$	0	$6\frac{1}{2}$	1.0	$10\frac{1}{2}$	27
3	0	7	1.5	11	32
$3\frac{1}{2}$	0	$7\frac{1}{2}$	2	$11\frac{1}{2}$	36
				12	40

is a fair amount of ice present, and the small rise of 3° C. at the end is due to the fact that with a very small amount of ice the stirring cannot keep all the water at the temperature

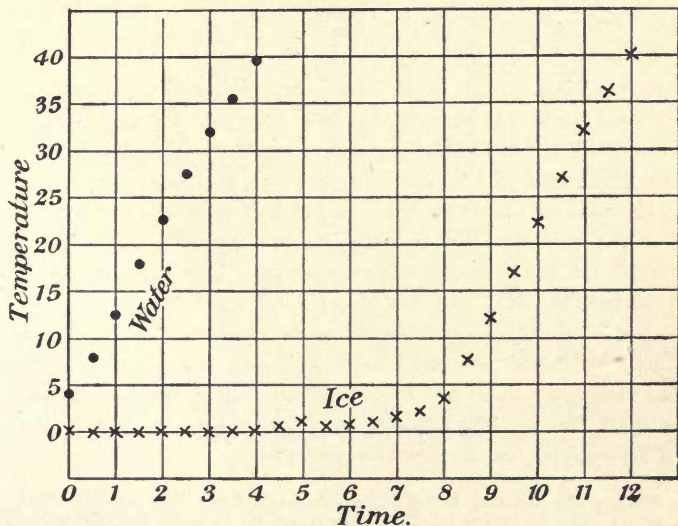


FIG. 58.



of that immediately in contact with ice.<sup>1</sup> Once the ice is melted the temperature rises at the rate of about  $5^{\circ}\text{C}$ . each half-minute; when the temperature of the water approaches that of the steam, the rate of supply of heat diminishes, as shown by the last two readings.

A second experiment, with an equal mass of water cooled to as low a temperature as possible, but with no ice, gave the following figures:—

Time.	Temp.	Time.	Temp.
mins.	$^{\circ}\text{C}$	mins.	$^{\circ}\text{C}$
0	4	2	22.5
$\frac{1}{2}$	8	$2\frac{1}{2}$	27.5
1	13	3	32
$1\frac{1}{2}$	18	$3\frac{1}{2}$	35.5
		4	39.5

The early readings of this again correspond to a rate of rise of temperature of just under  $5^{\circ}\text{C}$ . per half-minute.

Thus, while ice is melting heat is being supplied to it, but the resulting water is at much the same temperature; in our case we had to supply this heat for just over eight minutes to melt all the ice. Calling the mass of ice  $x$  gms. (this being also the mass of the resulting water), the heat was supplied at the rate of about  $5x$  calories per half-minute, and therefore in eight minutes  $80x$  calories were supplied. Thus to melt  $x$  gms. of ice requires something like  $80x$  calories (strictly speaking, the  $80x$  calories also raised the temperature of the water  $3^{\circ}$ , so that  $77x$  calories were used in melting the ice; since, however, we have neglected the water equivalent of the vessel, we shall not be far out in calling the heat required to melt the ice  $80x$  calories, and the value is only intended to be rough), or 80 calories per gm.

<sup>1</sup> Since the heat is being communicated from the outside through water to the ice, part of the water must be at a slightly higher temperature than the rest, otherwise the transmission of heat would be infinitely slow. See Chapter on conduction of heat.

This behaviour of ice is characteristic of solids ; in order to turn a solid into a liquid, heat must be supplied although the resulting liquid is at the same temperature. Since this heat seems to disappear (i.e. there is no corresponding rise in temperature), it is spoken of as latent <sup>1</sup> (meaning hidden). In reality it is a case of transformation of energy, and when the liquid solidifies the latent heat is given out.

**Definition of Latent Heat of Fusion.**—The latent heat of fusion of a substance is the amount of heat required to turn unit mass of the substance from solid to liquid without change of temperature.

**Determination of the Latent Heat of Fusion of Ice.**—The method just described is only intended to give a rough value ; it happens to have come out to a value very near the truth, but could not be relied on to give very accurate figures, and is only intended as an illustration.

The determination is usually carried out by the method of mixtures as follows :—

A calorimeter is weighed, and is then about two-thirds filled with water and weighed again ; this gives the weight of the water. The temperature of the water should be about 6° or 7° above room temperature. The calorimeter is placed on corks and the temperature of the water carefully determined. Some ice, broken up into fairly small pieces, has previously been got ready. Ice is added to the water in the calorimeter one piece at a time ; the piece of ice should be roughly dried on a cloth or blotting-paper before adding, and the water thoroughly stirred. As soon as the piece of ice is melted another should be added ; the process should be continued until the temperature of the water is a few degrees below the room temperature.

This temperature is read carefully and the calorimeter and its contents are then weighed ; by this means the weight of

<sup>1</sup> This name is due to Black, who first noticed the effect. The experiment described above is similar in principle to an experiment performed by Black, but is much more rapid.

ice added is determined. The following figures obtained in an experiment will illustrate the procedure.

Room temperature =  $17^{\circ}$  C.

Weight of copper cal.	. . . . .	= 192 gms.
Weight of cal. + water	. . . . .	= 649 gms.
∴ weight of water	. . . . .	= $\overline{457}$ gms.
First temperature of water	. . . . .	= $\overline{26.5^{\circ}}$ C.
Final temperature of water	. . . . .	= $13.5^{\circ}$ C.
Weight of cal. after adding ice	. . . . .	= 714 gms.
∴ weight of ice	. . . . .	= 65 gms.
Water equivalent of calorimeter	. . . . .	= 19 gms.
		(about).

Considering the water originally in the calorimeter 457 gms. of water + the calorimeter have cooled from  $26.5^{\circ}$  C. to  $13.5^{\circ}$  C.

∴ they have given out—

$$(457 + 19) \times 13 \text{ calories} \\ = 6,188 \text{ calories.}$$

Now this heat has been employed in two operations:—

- (1) Turning 65 gms. of ice at  $0^{\circ}$  C. to water at  $0^{\circ}$  C.
- (2) Raising the temperature of this 65 gms. of water which comes from the ice from  $0^{\circ}$  C. to  $13.5^{\circ}$  C.

But this last operation requires  $65 \times 13.5$  calories  
= 877 calories.

∴ 6,188 calories have been used in melting 65 gms. of ice without change of temperature and supplying a further 877 calories.

∴ To melt 65 gms. of ice requires . . . . . 5,311 calories  
∴ „ 1 gm. „ „ . . . . . 82 calories  
(to nearest whole number).

So that the latent heat of fusion of ice is 82 calories per gm.

The above experiment can be trusted to about 4 per cent.

The most accurate determinations give a value rather under 80 calories per gm. ; that is to say, nearer 80 than 79.

**The Melting-point of a Solid.**—If we take a piece of ice at a low temperature and gradually heat it, we reach a temperature at which it begins to melt. We have here an abrupt change ; there is no gradual softening of the ice ; it is either hard ice or liquid water, and the change takes place at a

perfectly definite temperature (but see page 142 on the influence of pressure), and while the change is going on the temperature remains constant. As we have already seen, change in volume occurs, and there is an absorption of heat without rise of temperature; moreover the specific heat of ice is quite different from that of water.

A large number of solids behave in the same way and melt at some definite temperature with an abrupt change in volume and an absorption of heat. Some however, mixtures such as paraffin wax and amorphous substances, do not have a perfectly definite melting-point; the solid softens and gradually passes into the liquid form, so that it is only possible to give a range of temperature within which melting occurs, and not a definite melting-point (see page 142).

In the case of solids with a definite melting-point, the liquid if cooled will, under ordinary conditions, freeze or solidify at the same temperature as that at which the solid melted; the latent heat is given out again and the temperature remains constant while the change is going on.

**Super-cooled Liquids.**—If water is cooled slowly and very carefully it is possible to get it to a temperature well below  $0^{\circ}$  C. without its freezing. If, however, it is then shaken, or better, if a fragment of ice is dropped in, the water at once freezes and the temperature rises to zero. The water below  $0^{\circ}$  C. is said to be super-cooled, and all substances with definite melting-points exhibit this phenomenon. It should be noticed that the introduction of a fragment of some other solid into a super-cooled liquid will not necessarily bring about solidification; the only certain way is to introduce a fragment of its own solid. Thus, the only true test as to whether a liquid is at its freezing-point is to see if it can remain in contact with its solid for an indefinite period without change occurring.

Although liquids can be super-cooled it does not seem possible to heat a solid above its melting-point; for this reason, although melting-point and freezing-point of a substance are frequently used as alternative terms, it is usual

to define  $0^{\circ}\text{C}$ . as the temperature at which pure ice melts, rather than that at which pure water freezes, as there is then no possibility of ambiguity.

### Determination of the Melting-point of a Solid.

A method suitable for cases where only a small quantity of the substance is available, and one which with skilled observers gives good results is as follows.

A small capillary tube (made by drawing out quill tubing) closed at the lower end contains some of the solid. It is fastened to the bulb of a thermometer by rubber bands and the thermometer placed in a beaker of water<sup>1</sup> as shown in Fig. 59, so that the upper end of the capillary is above the water. The beaker is gently heated and the water well stirred; as soon as the solid is seen to melt (which is noticed because it then becomes more transparent) the temperature is noted. The water is allowed to cool and the temperature at which the substance solidifies again is noted. If the experiment is performed with care this should not differ by more than a degree or two from the first

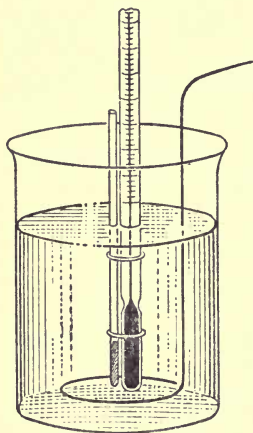


FIG. 59.

temperature; in this case the mean of the two temperatures may be taken as the melting-point.

A more accurate method, but one which takes a much longer time, is as follows:—

**Determination of the Melting-point of a Solid by the Method of Cooling.**—This method makes use of the latent heat of fusion. The apparatus described below is suitable for a laboratory determination when the melting-point is not

<sup>1</sup> This only applies to solids having a melting-point below  $100^{\circ}\text{C}$ . Other liquids can be used if the melting-point is above  $100^{\circ}\text{C}$ ., but the method is not very suitable for such cases.



too high. The method can, however, be adapted to meet the case of solids with high melting-points, such as metals and alloys; in that case the temperature measurement would be done by a thermo-couple or some such means.

A quantity of the solid is placed in a test tube,<sup>1</sup> and gently heated until it is all melted; it is then heated until its temperature is about 20° or 30° above the melting-point. (This temperature is estimated and care is required to avoid heating the liquid to a temperature above the range of the thermometer.) The test tube is then placed inside a larger tube, as shown in Fig. 60, a thermometer is suspended with its bulb in the liquid; the thermometer bulb must be covered by the liquid and must not touch the bottom of the tube. The amount of substance taken should be enough to cover the bulb easily; a large excess means that the experiment will take a very long time. A stirrer is also placed in the liquid.

The hot liquid is then allowed to cool, and the reading of the thermometer is noted every minute; constant stirring being maintained. At first the temperature falls fairly rapidly, as the tube is losing heat to its surroundings; but as soon as the liquid begins to solidify the latent heat of fusion is given out and this balances the heat lost to the surroundings. The result is that the

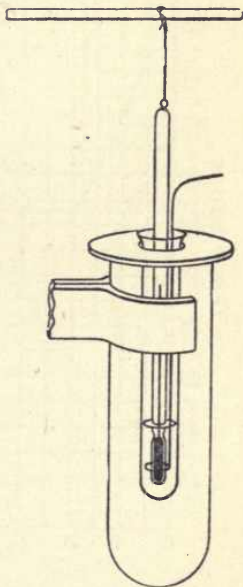


FIG. 60.

<sup>1</sup> The size of the tube is chosen to give a suitable rate of cooling. The smaller the tube the more rapidly will the temperature fall; it must, however, be large enough for a stirrer. In the experiment described, the inner tube was 6 inches  $\times$   $\frac{3}{4}$  inch and the outer 8 inches  $\times$  2 inches. An outer tube is essential to avoid disturbances in the rate of cooling which would give a misleading appearance to the results.

temperature remains constant. When all the liquid has solidified there is no more latent heat to balance the loss to the surroundings and the temperature then begins to fall again. A graph is plotted, showing the variation of temperature with time.

Fig. 61 shows the graph obtained with a specimen of phenol.

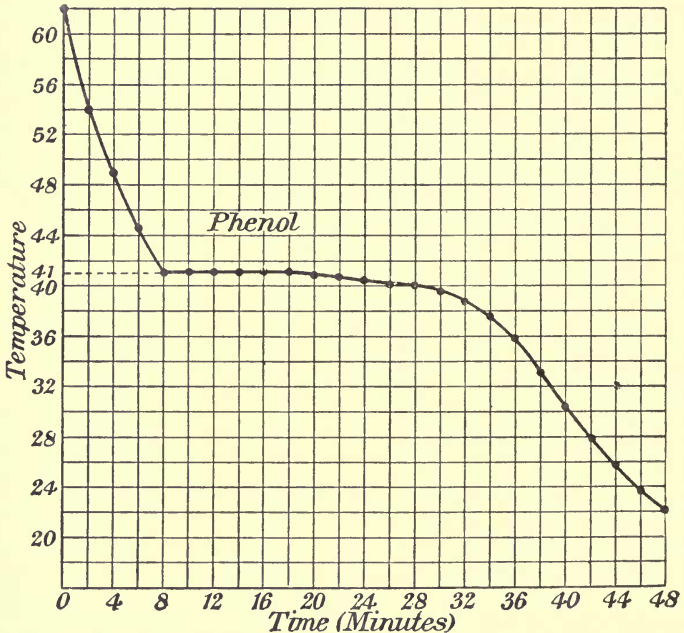


FIG. 61.

It will be seen that the temperature falls rapidly until at the 8th minute it has dropped to  $41^{\circ}\text{C}$ . At this stage it remained constant for twelve consecutive readings. At about the 20th minute so much of the phenol had solidified that stirring was no longer possible. The temperature then begins to fall; at first very gradually. The first gradual fall is probably due to the impossibility of stirring; at this stage most of the

substance is solid so that the lower part of the thermometer bulb is in contact with solid, the outer part of which is beginning to cool, while the upper part of the bulb is surrounded by the last remaining liquid, still at  $41^{\circ}\text{C}$ . The mean temperature of the bulb's surroundings is thus slightly below  $41^{\circ}\text{C}$ . The fall of temperature soon becomes unmis-

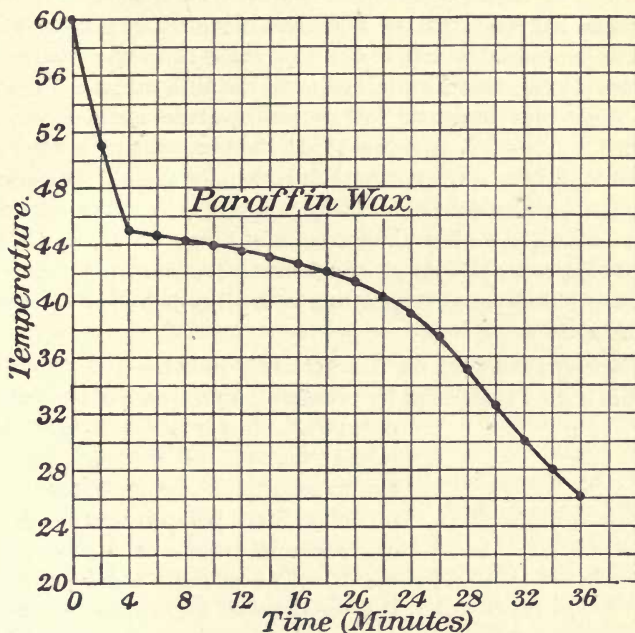


FIG. 62.

takable and we get the ordinary cooling curve of a hot solid. From an inspection of the graph we can at once see that the melting-point is  $41^{\circ}\text{C}$ .; we have rapid cooling until  $41^{\circ}\text{C}$ . is reached, then constant temperature for some time at  $41^{\circ}\text{C}$ ., and then a further fall.

Such a graph is characteristic of a pure single chemical substance (element or compound); there is one sharply-

defined melting-point. In the case of substances which are not single substances but are mixtures such as fats and waxes, a different result is obtained. Fig. 62 shows the graph obtained with paraffin wax in the same apparatus as in the previous experiment. Here it will be seen that the temperature falls rapidly until it reaches  $45^{\circ}\text{C}$ . At this stage the rate of fall of temperature abruptly diminishes, but the thermometer readings do not remain constant for several consecutive minutes. It is not a question of want of stirring, because stirring was maintained until the 10th minute. There is a slight but irregular fall of temperature until  $42^{\circ}\text{C}$ . is reached. After falling below  $42^{\circ}\text{C}$ . the temperature continues to fall rapidly and the curve then resembles the phenol curve. Thus there is no definite melting-point for the paraffin wax; solidification is taking place over the range  $45^{\circ}\text{C}$ . to  $42^{\circ}\text{C}$ .

In some cases the graph can be seen to develop a number of horizontal steps, corresponding to melting-points of different constituents.

**Effect of Pressure on the Melting-point.**—The melting-point of a solid is affected by pressure; in the case of ice which

occupies a larger volume than its liquid, increase of pressure lowers the melting-point, while in the case of solids like paraffin wax increase of pressure raises the melting-point.<sup>1</sup> The effect is not large; in the case of ice, an increase of pressure of one atmosphere lowers the melting-point by about  $0.0076^{\circ}\text{C}$ . This lowering of the melting-point is well illustrated by the following experiment (Fig. 63):—

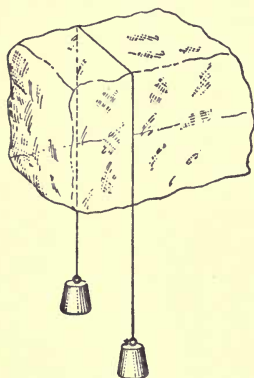


FIG. 63.

A large block of ice is placed on two supports, and round the middle of it is placed a loop of thin wire from which

<sup>1</sup> This effect can be predicted from considerations of energy, see Chapter XXII, p. 333.

heavy weights are suspended. Since the area of the wire in contact with the ice is small, the weight produces a large pressure per unit area under the wire. The ice under the wire melts, and the wire sinks in ; the water formed, flowing round the wire, is released from pressure and freezes again. This goes on, so that in course of time the loop of wire passes right through the ice and falls off, but leaves the block of ice in one piece ; a few small air bubbles imprisoned by the freezing water mark the plane along which the wire has cut.

This melting under pressure and subsequent freezing together again is spoken of as "regelation." It is well illustrated by the behaviour of snow. Thus in making a snowball the snow is pressed together and released to make it "bind" ; the formation of a hard mass under the heel of the boot when walking on snow is also an example of this effect. If the temperature is much below freezing-point the snow will not bind ; in other words, the pressure is not enough to bring the melting-point as low as the existing temperature.

When a skater gets on to an edge, the area of the skate blade in contact with the ice is very small, and hence the pressure per unit area is large and the ice under the blade melts, enabling the blade to sink in a little ; when it has passed the water freezes again, so that there is no groove left behind, but only a few imprisoned bubbles of air showing where the skate has been, unless the ice is thawing. If the temperature is very much below freezing-point, the skate will not bite ; in other words, before it can sink in appreciably, the area in contact with ice is such that the weight of the body does not supply enough pressure to lower the melting-point to the required extent. It may be noted that the slipperiness of ice is due to this melting under pressure ; very cold ice is not slippery.

Unlike water, the majority of substances occupy a greater volume in the liquid than in the solid state, and consequently the melting-point is raised by pressure. The Earth itself probably supplies an example of this. It is well known that the temperature of the earth increases with the depth below



the surface, and if this increase is maintained the temperature at depths quite small in comparison with the radius of the earth must be above the melting-point of any known substance. All the evidence goes to show that the earth is solid,<sup>1</sup> and it is concluded that the enormous pressure of the layers above must raise the melting-point sufficiently to keep the interior solid even at these temperatures. If for any reason the pressure is released anywhere, liquefaction may take place and volcanic phenomena occur.

**The Freezing-point of Solutions.**—The freezing-point of a solution is lower than that of the pure solvent. For example, the freezing-point of a solution of salt in water is lower than  $0^{\circ}\text{C}$ .; the exact temperature depends on the strength of the solution. The freezing-point of a solution of anything else in water is also lower than  $0^{\circ}\text{C}$ .; different substances produce different effects as regards the lowering. It should be noted that when a solution freezes pure ice separates out, leaving the solution more concentrated; if the freezing is continued, the solution may become so concentrated that it reaches the saturation point when the dissolved substance begins to separate also.

**The Action of Ice and Salt—Freezing Mixtures.**—We have several times made use of a mixture of ice and salt in order to obtain temperatures lower than  $0^{\circ}\text{C}$ .; we are now in a position to get some idea of what happens. This is a particular case of a general principle depending on latent heat.

In order to simplify the matter, let us consider what would happen if we add ice to a solution of salt. Suppose we had a solution containing about 14 per cent. of salt; the freezing-point of such a solution is  $-10^{\circ}\text{C}$ . If the solution is at  $-10^{\circ}\text{C}$ . and ice at  $-10^{\circ}\text{C}$ . is added, nothing much can happen; we have a solid in contact with its liquid at the freezing-point, and there is no reason why any change should

<sup>1</sup> For example, if the interior were liquid something equivalent to tides would be produced; but the occurrence of earthquakes regularly twice a day is not a universal experience.

take place. But suppose they were both at  $0^{\circ}\text{C}$ .; the solution is now in contact with ice at a temperature above its freezing-point; consequently some ice would melt. But in order to do this it must get its latent heat of fusion from somewhere, and it does it by taking heat from the solution and itself and thereby lowers the temperature, which falls below  $0^{\circ}\text{C}$ . This would go on until all the ice had melted or the temperature had fallen to the freezing-point.<sup>1</sup>

Thus the solution in contact with ice has caused a lowering of temperature because it makes the ice change its state from solid to liquid.

This effect is quite a general one and is not confined to ice. When any solid dissolves in water (or other solvent) it is passing from the solid to the liquid and therefore there should be a fall in temperature; good examples of this are furnished by ammonium nitrate and sodium thio-sulphate ("hypo" of the photographer) which when dissolved in water cause a considerable fall in temperature. When solid carbon dioxide is dissolved in ether, a temperature below  $-100^{\circ}\text{C}$ . can be obtained. It does not follow that a fall of temperature will result in all cases; there is also the action between the solid and liquid to consider, and it may happen that the heat evolved in this is greater than that absorbed to furnish the latent heat of fusion, so that on the balance there is a rise in temperature—potassium hydroxide dissolved in water is a good example.

When salt is added to ice a certain amount of solution occurs, and then the ice melts as already explained; both the solution of the salt and the melting of the ice involve absorption of heat. Thus a fall of temperature results. Absorption of heat can only go on as long as a change of state is proceeding. The temperature cannot fall below about  $-20^{\circ}\text{C}$ ., because a solution of such strength that its freezing-point is as low as this is also saturated with salt at that temperature, so that it is impossible to get a salt solution

<sup>1</sup> Since the melting ice would make the solution more dilute, the freezing-point would now be above  $-10^{\circ}\text{C}$ .

with a freezing-point lower than this. The important thing to remember is, that the effect of the salt is to cause the ice to melt. For this reason it is a precisely similar operation when salt is spread on a frozen pavement in order to get the ice to melt: the ice does melt, but the temperature is lowered.

Ice and salt form quite a good freezing mixture, but ice and calcium chloride do better, since calcium chloride is excessively soluble.

## CHAPTER X

### CHANGE OF STATE—LIQUID TO VAPOUR

If we take some water in a flask and heat it over a burner, the temperature rises at first ; ultimately a stage is reached when the water boils and no further rise in temperature takes place. All that happens is that the water is converted to a colourless vapour.<sup>1</sup> Here we have another change of state, and in some respects the phenomena are similar to those accompanying the change from solid to liquid.

In the first place there is a very large volume change ; 1 c.c. of water forms about 1,700 c.c. of steam under atmospheric pressure. The engineer's rough rule is that a cubic inch of water forms a cubic foot of steam. Secondly, a large amount of heat is absorbed in turning the water to steam. As a rough illustration the following experiment may be quoted :—

A flat-bottomed flask is weighed empty, and then partly filled with water and weighed again. The flask is fitted with a cork through which pass a

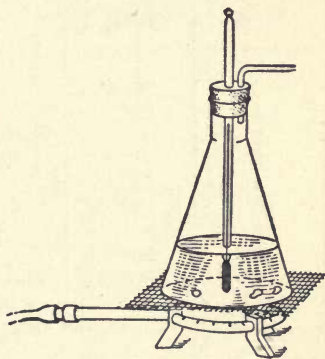


FIG. 64.

<sup>1</sup> When the vapour comes in contact with the cold air it condenses to a visible cloud which is really a collection of very small particles of water. This cloud is sometimes incorrectly spoken of as steam. Steam itself is invisible as long as it is hot, e.g. in the upper part of the flask ; when it becomes visible it is no longer steam but water.

thermometer and a short outlet tube (Fig. 64). A few pieces of broken brick are put in to assist steady boiling (see page 160); these are weighed with the empty flask. The flask is placed on a gauze on a ring burner (a bunsen would not supply heat at a rate sufficient for satisfactory results) and the reading of the thermometer noted every minute. When the water boils the heating is continued for some time, and then the flask is removed and placed in a dish of cold water. When it is sufficiently cooled the outside is dried, the cork removed, and the flask and contents weighed. The following figures illustrate what happens :—

Weight of empty flask . . . . .	85	gms.
„ „ flask + water . . . . .	470	gms.
Final weight of flask + water . . . . .	410	gms.
Original weight of water	= 385	gms.
Weight of water boiled away	= 60	gms.

Time.	Temp.
m.ins.	
0	20° C.
1	28°
2	}
3	
4	62° C.
5	73°
6	84°
7	95°
7½	100° C.
14½	

Surface of mercury hidden by the cork.

Water boils. It is allowed to go on boiling until flask removed.

Now, in three minutes the temperature went from 28° to 62° C., or about  $11\frac{1}{3}$ ° per minute. The rate of rise afterwards was 11° per minute. We may assume that the average rate (neglecting the first minute) was about 11° per minute.

Since there were 385 gms. of water the burner was supplying about  $11 \times 385 = 4,235$  calories per minute to the water. After the water boiled, heat was supplied for a further seven



minutes, and the result was that 60 gms. of water boiled away.

Thus  $7 \times 4,235$  calories were required to turn 60 gms. of water at  $100^\circ$  to steam.

Thus the water required  $\frac{7 \times 4,235}{60}$  calories per gm. to turn it to steam,

= 494 calories per gm., or roughly 500.

Just as in the case of fusion, this heat is spoken of as latent.

Other liquids behave in the same way, but of course require different amounts of heat.

**Definition of the Latent Heat of Vaporization of a Liquid.**—The latent heat of vaporization of a liquid is the amount of heat required to turn unit mass of the liquid to vapour without change of temperature.

**Determination of the Latent Heat of Vaporization of Water or the Latent Heat of Steam.**—The method described above must not be regarded as in any sense accurate. To obtain a reliable value for the latent heat a method somewhat similar to that employed in the case of ice is used. The idea is to pass steam into a known weight of water in a calorimeter and measure the amount of heat given out by the steam in condensing. The calorimeter, of known weight and containing a known weight of water, is mounted on three corks as before. In the meantime a boiler of the form shown

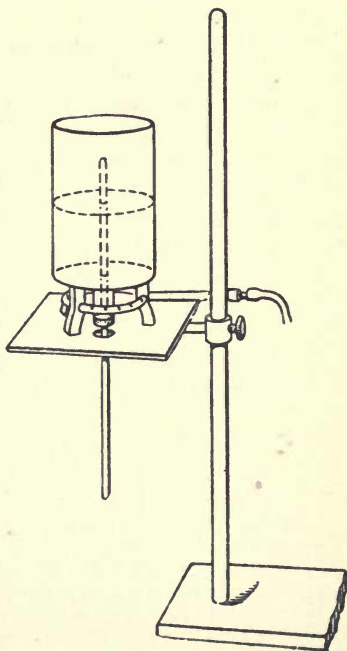


FIG. 65.

in Fig. 65 is got ready. It is made up of a copper vessel with a narrow neck fitted with a cork; through the cork passes a glass tube which reaches nearly to the end of the vessel. The vessel is half filled with water and placed on a ring burner as shown. The burner stands on a sheet of asbestos (with a small hole for the tube) carried on the ring of a retort stand. The temperature of the water in the calorimeter is noted, and then when steam is issuing freely from the boiler the latter is transferred bodily by means of the stand and placed with the end of the tube under the surface of the water in the calorimeter. When the temperature of this water has been raised about 15 or 20° (but not more <sup>1</sup>) the boiler is removed, the water is thoroughly stirred and the highest temperature it attains is noted. The calorimeter and its contents are now weighed,<sup>2</sup> to find out the weight of steam which has been condensed. The following figures illustrate the method of calculation:—

Weight of calorimeter + thermometer . . . . .	210	gms.
"          "          "          + water . . . . .	778	gms.
Weight of water . . . . .	<u>568</u>	gms.
Weight of calorimeter + thermometer + water +		
condensed steam . . . . .	796	gms.
Weight of steam condensed . . . . .	18	gms.
Initial temperature of water . . . . .	17°	C.
Highest temperature reached . . . . .	35.5°	C.
Water equivalent of calorimeter . . . . .	19	gms.

Heat received by calorimeter and water—  
 $= (568 + 19) (35.5 - 17) = 587 \times 18.5 = 10,860$  calories.

If  $L$  is the latent heat of steam, the heat given out by the steam in condensing at 100° C. is  $18L$  calories.

<sup>1</sup> If the temperature gets much above 35° C. not only is the cooling correction serious, but considerable evaporation takes place, making the apparent weight of the steam too small. The writer has made many experiments to verify the point.

<sup>2</sup> It is best to keep the thermometer in for all the weighings; if it is taken out it may easily remove nearly a gramme of water, and since the total weight of steam is not large, this forms a serious error.

Heat given out by the 18 gms. of water formed in cooling to  $35.5^{\circ}$  is—

$$\begin{aligned} 18(100 - 35.5) &= 18 \times 64.5 = 1,160 \text{ calories} \\ 18L + 1,160 &= 10,860 \\ 18L &= 9,700 \\ L &= 539 \text{ calories per gramme.} \end{aligned}$$

The object of having the boiler of the form shown is to avoid as far as possible condensation taking place before the steam gets to the calorimeter. If water is carried over with the steam it is all weighed and counted as steam, and serious errors result. An alternative method is to have some form of steam trap on the tube, but the writer finds the boiler as described to be more satisfactory; it is easy to move, and it is better to move the boiler than the calorimeter.

The method given above cannot be relied on to more than about 5 per cent. The weight of steam condensed is small compared to the weight of water in the calorimeter, and consequently this weight is determined by the difference between the weights of two large quantities of water.<sup>1</sup> Moreover, it is not very satisfactory to have steam blowing over the surface of the water as the nozzle is introduced and removed, while a stoppage of the steam might result in some water being drawn into the tube. For these and other reasons, in accurate work the steam is condensed in a spiral tube of metal contained in the calorimeter and is not allowed to mix with the water; this method is also essential for finding the latent heat of vaporization for liquids other than water. Very elaborate and accurate experiments were performed by Regnault; a much simpler and quite accurate apparatus is that due to Berthelot. The apparatus is shown in section in Fig. 66. The flask has a wide tube down the centre which is connected to the metal spiral and reservoir. It is heated

<sup>1</sup> One may be permitted to describe an operation of this sort as "weighing a haystack, putting a needle in, and weighing again in order to find the weight of the needle."

by a gas burner in the form of a circle with a gap in it, so that it can be withdrawn. The calorimeter is protected by a thin wooden screen covered with a sheet of gauze. The vapour passes down the wide tube into the spiral and condenses in the reservoir.

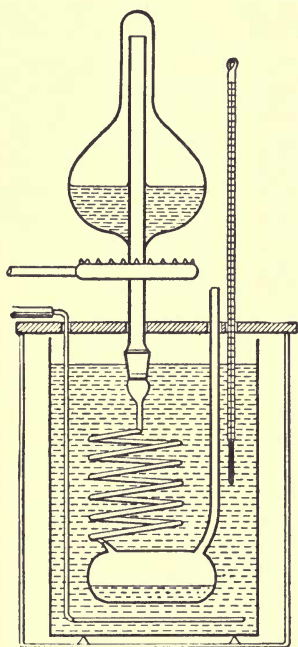


FIG. 66.

Since heat is conducted down this tube, observations are made on the rate of rise of temperature of the water in the calorimeter before the vapour comes over. The calorimeter contains some 800 or 900 gms. of water, and the rise in temperature was usually  $3^{\circ}$  or  $4^{\circ}$ . The time occupied is from two to four minutes. The apparatus was primarily intended for determination of the latent heat of vaporization of liquids other than water; M. Berthelot tested its accuracy by finding the latent heat of steam with it and as his results agreed closely with those of Regnault he regarded its accuracy as established.<sup>1</sup>

The value obtained by Regnault for the latent heat of vaporization of water at  $100^{\circ}\text{C}$ .<sup>2</sup> is just under 537 calories per gm. Callendar gives 539.3 calories per gm.

### Effect of Pressure on the Boiling-point of a Liquid.—

The temperature at which a liquid boils is determined by the pressure to which it is exposed. It is not a question of minute effects as in the case of the melting-point; at a

<sup>1</sup> Berthelot, *Comptes Rendus*, LXXXV, 646, 1876.

<sup>2</sup> The latent heat of vaporization is greater at low temperatures than at high; it vanishes at the critical temperature (see page 264).

pressure of two atmospheres the boiling-point of water would be about  $121^{\circ}\text{C}$ . instead of  $100^{\circ}\text{C}$ . The boiling-point of any liquid is raised by increased pressure; this will readily be understood when the meaning of boiling is considered (page 159).

The effect is well illustrated in the case of water by using a Marcet boiler or Papin's digester (Fig. 67). This is a stout copper vessel to which a

strong lid is attached by studs. The lid is fitted with a pressure gauge, a lever safety valve, an outlet tube with a tap and a thermometer pocket. A thermometer pocket is simply a metal tube closed at the lower end, and reaching well down into the vessel; the thermometer is placed in the pocket and so is not exposed to the pressure inside the vessel. The vessel is partly filled with water and the weight on the safety valve lever is put in such a position that the valve will "blow off" at a suitable pressure. The water is boiled by means of a ring burner or large bunsen,

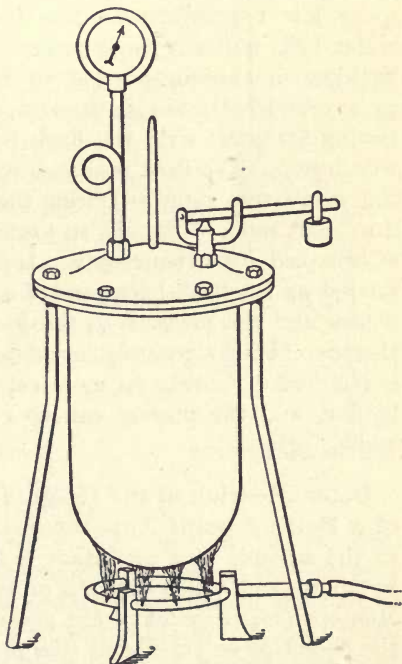


FIG. 67.

and when the safety valve is blowing off the pressure on the gauge is noted and the temperature as given by the thermometer. The weight of the safety valve is then moved so as to blow off at a higher pressure and the water boiled again. In this way a series of readings may be obtained.



It will be noticed that as the pressure is increased the boiling-point is raised ; at a pressure of 200 lb. per square inch <sup>1</sup> the boiling-point is about 193° C.

In the same way, under low pressures, the boiling-point of water is below 100° C. This may be illustrated by boiling water in a Wurtz flask with its side tube connected to a vacuum pump (an ordinary water-filter pump does very well). It will be found that it is possible to get the water to boil at quite low temperatures. The low temperatures at which water boils under reduced pressure is also illustrated by the well-known experiment due to Franklin. Water is boiled in a round-bottomed flask, and after the steam has been issuing for some time the flask is corked up and the flame withdrawn. The flask is then inverted and supported on the ring of a retort stand. During the boiling, the issuing steam drove out most of the air, so that the space above the water is occupied by vapour only. If now a little cold water is poured on the flask by means of a sponge, some vapour condenses and the pressure in the flask is reduced. The water thereupon boils vigorously for a few minutes until the pressure is restored. Pouring on more cold water results in renewed boiling, and the process can be continued for quite a long while.

**Determination of the Heights of Mountains by Means of a Boiling-point Apparatus.**—The atmospheric pressure at the summit of a mountain is less than that at sea-level by an amount which depends on the height of the mountain. Hence a measurement of the pressure at the summit enables the height to be calculated (the pressure at sea-level or some known elevation must be known, since the atmospheric pressure varies from day to day). A mercury barometer is the most accurate means of measuring the pressure, but a determination can be made by finding the boiling-point of

<sup>1</sup> This is the actual or absolute pressure, not 200 lb. per sq. inch above atmospheric ; it would be about 185 lb. per sq. inch above the atmospheric.

water. The boiling-point of water at different pressures has been determined, and tables have been drawn up; thus if the boiling-point is known, the pressure can be ascertained. This is the origin of the term hypsometer (height measurer) for a boiling-point apparatus. A hypsometer is not so accurate as a mercury barometer, but it is much more portable; in any case it serves as a useful check on an aneroid, and is probably more reliable if the determination is carried out carefully.

**Evaporation.**—Liquids can pass into vapour without boiling. For example, if a shallow dish of water be left for some time in a room the water will ultimately disappear; another well-known example is furnished when wet clothes are put out in the open to dry. In this case evaporation takes place, and in order to get a clear idea of what happens it will be convenient to put down the known facts first, and then consider the experimental work which established them. Our knowledge of the facts is founded on the work of Dalton.

Let Fig. 68 represent a small dish of water underneath a large bell jar. Let us suppose that the space under the bell jar is completely exhausted of air. - Then some of the water will turn into vapour, and this will go on until the pressure of the vapour inside the bell jar attains a certain value depending on the temperature (this assumes that there is enough water for this stage to be reached without all the water being used up). For example, if the temperature were  $15^{\circ}\text{C.}$ , evaporation would go on until the pressure was 12.8 mm. of mercury. The space is then said to be saturated with vapour, and 12.8 mm. is the saturation pressure of water vapour at  $15^{\circ}\text{C.}$  If the bell jar were full of air or any other gas (so long as it had no chemical action with water) the evaporation would

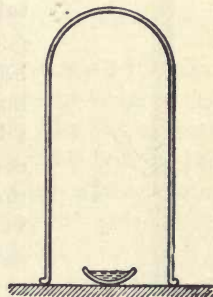


FIG. 68.

still go on until the pressure of vapour was 12.8 mm.; i.e. if the pressure of air were originally 760 mm. the total pressure would be 772.8 mm.<sup>1</sup> The only difference would be that it would take much longer to reach the steady stage, but the final result would be the same. It may be noted that evaporation takes place only at the surface (see page 276). The saturation pressure increases with temperature; thus, at 20° C. it is 17.5 mm. for water.

If, when the steady state has been reached, the volume of the space were altered, evaporation or condensation would take place until the pressure of vapour got back to its saturation pressure. If, however, the volume were increased very much a stage would be reached when all the water had evaporated; further expansion would result in the space being unsaturated. The passage from liquid to vapour involves the absorption of heat, as we have already seen; if this is not supplied from the surroundings the liquid will cool as it evaporates.

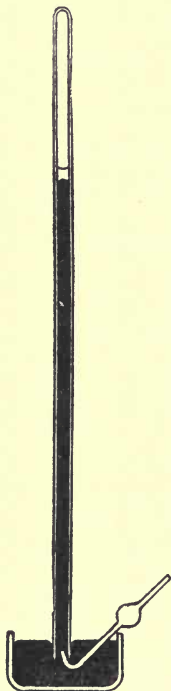


FIG. 69.

#### Measurement of Vapour Pressures.—

The most straightforward way of measuring the vapour pressure of a liquid at moderate temperatures is to make use of a barometer tube. For example, to measure the vapour pressure at room temperature, a barometer tube is filled with mercury and inverted in a bowl of mercury. The height of the mercury column (measured from the surface of the mercury in the tube to the surface of the mercury

<sup>1</sup> This result, known as Dalton's Law, that the pressure of the vapour is independent of the substances already occupying the space, is found not to be strictly true at high total pressures.

in the bowl) is noted. A little of the liquid is then introduced by means of a pipette bent at the end as shown in the section Fig. 69.

The liquid rises to the top of the column and evaporates in the vacuous space; enough liquid must be sent up to leave some remaining when the evaporation is complete. The pressure of the vapour drives the column down a certain amount; the height of the column is measured, and the difference between this height and the original gives the pressure of the vapour. If there is a large amount of liquid on the top of the mercury, a correction must be made for the pressure due to the weight of it; if the length of the liquid column is  $l$  and the specific gravity  $d$ , it will be equivalent to an extra height of mercury of  $\frac{ld}{13.6}$ , taking 13.6 as the Specific Gravity of Mercury. Now, suppose the original height were 760 mm. and the height afterwards was 748 mm., the pressure of the vapour would be 12 mm. of mercury, since the atmosphere is now supporting a column of mercury 748 mm. + the pressure of the vapour. It can be seen that adding more liquid does not alter the pressure of the vapour (correction must be made for the extra column of liquid).

By having several barometer tubes the vapour pressure of various liquids can be measured. Thus at 15° C. the vapour pressure of water is 12.8 mm. of mercury; the vapour pressure of alcohol is 32.6 mm. of mercury; the vapour pressure of ether is about 357 mm. of mercury.

**Vapour Pressures at Different Temperatures.**—The vapour pressure of a liquid increases as the temperature is raised; this is well illustrated in the case of water by means of the apparatus described below, which can also be used for other liquids. Fig. 70a shows the arrangement for temperatures below 100° C.

B is a straight barometer tube which is connected to a tube C of the same bore but open at the top. The arrangement forms a syphon barometer, and into the Torricellian vacuum some water has been introduced. The two tubes

are surrounded by a wide tube, which is filled with water, the outlet D being closed with a clip.

The water in the jacket tube can be raised to any convenient temperature by blowing in steam, the water is then thoroughly stirred, the temperature noted, and the height  $h$  measured.

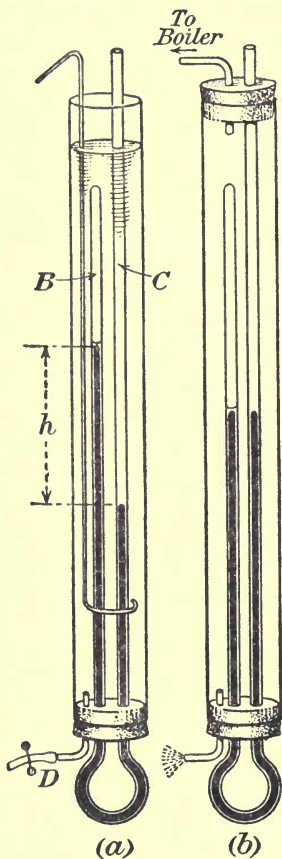


FIG. 70.

The pressure of the vapour is then the pressure of the atmosphere minus pressure due to a column of mercury of height  $h$ . For rough work we can get the vapour pressure by simply subtracting  $h$  from the reading of the barometer in the room; for more accurate work the height  $h$  must be corrected for the density of the mercury at the temperature of the jacket.

By blowing in steam the water can be raised to a higher temperature, and in this way a series of readings can be obtained. It will be observed that the increase in vapour pressure is not proportional to the rise in temperature, but is more rapid at high temperatures.

The jacket is then emptied by opening D; a cork is fitted at the top as shown in Fig. 70b, and steam is passed through. It will then be observed that the mercury in the

two tubes comes to the same level (correcting for the weight of any water on the top of the mercury in the closed limb), so that *at the boiling-point*



*the pressure of the water vapour is equal to the atmospheric pressure.*

This result is most important, and will be found to be the case for all liquids ; for example, if we had alcohol in the tube B and passed vapour from boiling alcohol through the jacket, we should get the same effect. At temperatures above the boiling-point the vapour pressure would be above the atmospheric, so that the mercury in C would stand higher than that in B. We are now in a position to understand the meaning of boiling.

**Ebullition or Boiling.**—Suppose we have a beaker of water being heated by a burner. As the heat is supplied the temperature of the water rises. A certain amount of evaporation takes place at the surface, and faint clouds appear a little above the surface where the warm vapour has cooled in contact with air. This evaporation involves the supply of latent heat of vaporization, but the burner supplies heat at a rate which more than keeps pace with this (if it does not, a stage is reached where the vapour carries off all the available supply of heat and no further rise of temperature takes place) and the temperature continues to rise. During this stage some of the air or other gases dissolved in the water begins to come out and form small bubbles, which usually cling to the side of the vessel. But when the temperature is such that the vapour pressure is equal to the atmospheric, a new possibility comes in ; for bubbles of vapour can form within the liquid<sup>1</sup> and grow by evaporation. As these bubbles provide evaporating surfaces (from the liquid into the interior of the bubble) enough evaporation takes place to use up the whole heat supply ; more rapid supply of heat would merely give more bubbles. At this stage the liquid is said to boil, and the characteristic of boiling is the *formation of vapour at points within the liquid as well as at the free surface.*

<sup>1</sup> They require something to start on, which is furnished by some of the gas bubbles or a roughness on the side of the vessel ; they do not start in the midst of the liquid, but from some object.

Since the evaporation into the interior of the bubble has to overcome the pressure of the liquid on the outside, it is clear that the bubble cannot grow unless the vapour pressure is at least equal to this outside pressure. Hence the liquid cannot boil until the vapour pressure is equal to the atmospheric pressure. It therefore becomes obvious why the boiling-point depends on the external pressure.

**Delayed Boiling.**—If there are no suitable objects for the bubbles to start on, it is possible for the temperature of the liquid to be raised considerably above its proper boiling point; if a bubble is then formed it grows violently, and the effect known as “bumping” occurs. To prevent this, small pieces of a porous substance, such as pieces of broken brick, should be put into the liquid to form suitable nuclei for the bubbles (compare page 148).

**The Boiling-point of a Solution.**—The presence of a substance <sup>1</sup> dissolved in a liquid lowers the vapour pressure, so that if the vapour pressure is to attain the pressure of the atmosphere the solution has to be raised to a higher temperature than would be required for the pure liquid. In other words, the boiling-point of a solution is higher than that of the pure liquid. (It is this lowering of the vapour pressure which lowers the freezing-point, but the connection is not so obvious at first sight.)

**Determination of Boiling-points.**—The procedure depends on whether we are dealing with a pure liquid or a solution. The following experiments will make this clear.

A flask is taken, fitted with a cork through which pass a thermometer and an outlet tube. Some pure water is placed in the flask, together with a few pieces of broken brick. The thermometer is arranged to stand with its bulb an inch or

<sup>1</sup> We are here considering the case of substances which are not appreciably volatile, so that the vapour given off is that of the solvent only. With a solution of a volatile substance each lowers the vapour pressure of the other so that the resulting vapour pressure is lower than the sum of the vapour pressures of the two separate substances.

so above the surface of the water. The water is boiled, and when the steam is issuing freely and the reading of the thermometer is steady the temperature is noted. The experiment is repeated with bulb of the thermometer in the water; the temperature will be found to be much the same as before. It may be a trifle higher owing to delayed boiling or traces of dissolved substance.<sup>1</sup> These experiments are repeated using a solution of salt in water. It will be found that the temperature of the vapour is the same as it was for pure water,<sup>2</sup> while the temperature of the liquid may be several degrees higher.

Thus if we are determining the boiling-point of a pure liquid, the thermometer should be in the vapour; this will avoid any possibility of an error due to delayed boiling or other causes. An apparatus of the hypsometer type should be employed.

If we are determining the boiling-point of a solution the thermometer must be in the liquid, otherwise we shall get the boiling-point of the solvent, not of the solution.

**Determination of the Boiling-point of a Liquid when only a small quantity is available.**—A U-tube is taken, having one limb sealed and the other open (Fig. 71). It is partially filled with mercury as shown, and a few drops of the liquid introduced as shown at A. The tube is placed in a bath of some liquid of higher boiling-point, and the temperature gradually raised. A stage is reached when the mercury stands at the same level in each limb; the temperature at which this takes place is the boiling-point of the liquid A at the pressure of the atmosphere at the time of the experiment.

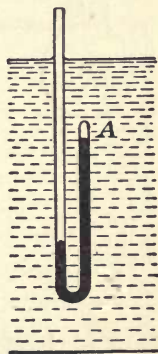


FIG. 71.

<sup>1</sup> There is also a smaller length of the thermometer stem exposed.

<sup>2</sup> If the first reading is taken with the thermometer in the solution some salt will remain on the bulb and make the vapour appear to have a higher temperature unless the bulb is carefully washed.

**Vapour Pressure of Liquids at High Temperatures. Regnault's Method.**—The pressure in the reservoir B (Fig. 72) was maintained at some definite pressure, as indicated by the manometer C, by pumping in or withdrawing air. The liquid was heated at A and ultimately boiled, the vapour condensing at D and flowing back to A. The thermometers<sup>1</sup> gave the temperature at which the liquid boiled under the pressure in the reservoir, i.e. the temperature at which the vapour pressure was equal to that registered by C. The pressure in B was then increased, and the reading of the thermometers gave the boiling-point under the new pressure. In this way Regnault determined the vapour pressure of

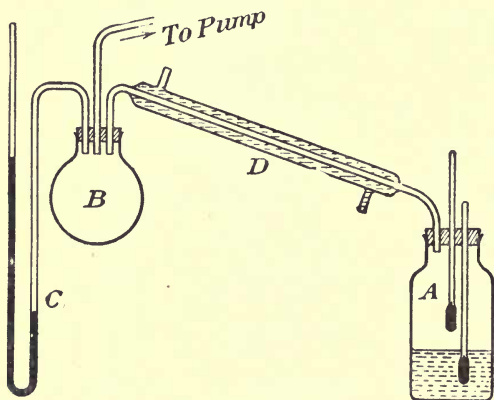


FIG. 72.

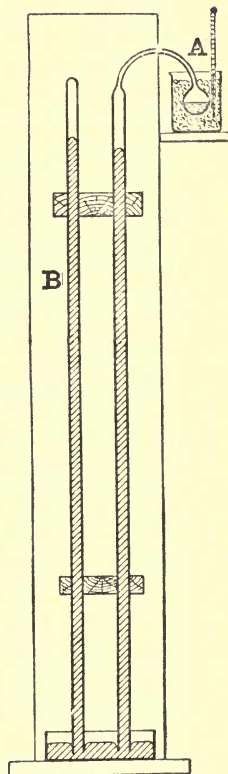


FIG. 73.

water at temperatures ranging from  $50^{\circ}$  C. to  $230^{\circ}$  C., at which latter temperature the pressure was 27 atmospheres.

**Vapour Pressure at Low Temperatures—Evaporation from Solids.**—Ice and many other solids have appreci-

<sup>1</sup> The thermometers gave the same reading, indicating an absence of delayed boiling.



able vapour pressures. Regnault determined the vapour pressure of ice by means of the apparatus shown in Fig. 73. The barometer tube is bent over and terminates in a bulb A which contains the ice. A is immersed in a freezing mixture which is liquid and well stirred. The solids have a definite vapour pressure corresponding to each temperature. The pressure of the atmosphere is read off on B.

**Sublimation.**—If a solid such as iodine is heated in a tube it will vaporize without liquefying and the vapour will condense back to solid in the upper part of the tube. Such a process corresponds to the distillation of a liquid and is known as sublimation.

**The Properties of an Unsaturated Vapour.**—The general behaviour of a vapour may be illustrated in the following way. Suppose we have a long barometer tube in a tall trough of mercury. Let a very small quantity of water or some other liquid, e.g. alcohol or ether, be introduced. Starting with the barometer tube at the bottom of the trough, let it be gradually raised. At first the mercury, with the liquid on the top, fills the tube; a stage is soon reached, as shown in Fig. 74, at which a space develops into which the liquid has evaporated. Here the height  $h$  is such that the difference between the barometer reading and  $h$  is equal to the vapour pressure of the liquid. As the tube is raised the mercury remains at the same height  $h$ ; the volume of the space is increased, but more liquid evaporates and the vapour pressure remains constant, as long as any liquid is left. But when all the liquid has gone, further raising of the tube results in the height  $h$  of the mercury increasing. The space is now unsaturated, and the unsaturated vapour behaves like any gas; as the volume is increased the pressure is diminished. It does not, however, obey Boyle's Law very accurately, but as the pressure diminishes the vapour approaches more nearly

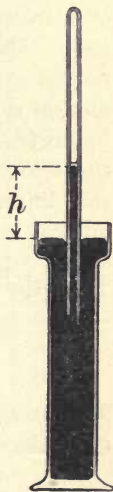


FIG. 74.



to obeying the Law. If the tube is lowered, the reverse process goes on; the pressure increases as the volume diminishes, until a stage is reached when the saturation pressure is reached and liquid begins to form.

If we take a gas like sulphur dioxide and compress it, a stage is reached at which the relation between pressure and volume deviates considerably from Boyle's Law, and if we go on compressing it the gas will ultimately liquefy. The process is precisely similar to that of the preceding paragraph, but the pressures involved are much greater; for example, at 15° C. sulphur dioxide requires a pressure of about 2.7 atmospheres to liquefy it and carbon dioxide about 55 atmospheres.

It is found, however, that at ordinary temperatures no amount of pressure will liquefy gases like hydrogen, oxygen, or nitrogen. Pressures up to 30,000 atmospheres have been used. Only when they are cooled to very low temperatures indeed can they be liquefied. There is, however, no fundamental difference between these gases and others, for it is found that for any gas there is a certain temperature, called the *critical temperature*, above which no amount of pressure will liquefy it. In the case of hydrogen and oxygen the critical temperature is very low.

Thus the critical temperature for hydrogen is	-234° C
„ „ „ „ sulphur dioxide is	155° C
„ „ „ „ carbon dioxide is	31.1° C
„ „ „ „ water is about	365° C

The question of the liquefaction of gases is dealt with in Chapters XVII and XIX.

**Cooling due to Evaporation.**—Since the change from liquid to vapour involves an absorption of heat, it follows that if a liquid evaporates and heat is not supplied, the liquid must take heat from itself and the surroundings. This may readily be illustrated in the case of a volatile liquid like ether. Some ether is placed in a flat-bottomed flask and the flask is placed on a block of wood; a few drops of water are put on the block

before the flask is put on. A stream of air is blown through the ether by means of foot bellows ; this causes rapid evaporation, and in a few minutes the water under the flask will be frozen, so that the block can be lifted by the flask.

Water can be made to freeze by its own evaporation ; to do this the evaporation must be rapid. Rapid evaporation can be brought about by having a dish of water in an exhausted enclosure and absorbing the vapour as fast as it comes off, so that the space does not become saturated. A few drops of water are placed in a watch-glass supported above a porcelain vessel containing concentrated sulphuric acid ; sulphuric acid has a strong affinity for water. The whole is placed under the receiver of a good air pump. The pump is worked and the water evaporates ; after a time the remaining water will freeze into a solid lump.<sup>1</sup>

Wollaston's cryophorus is an illustration of the same effect. This instrument is a glass tube with a bulb at each end (Fig. 75). It contains some water, and before sealing off it is exhausted, so that the space not occupied by water contains water vapour only. One bulb, B, is placed in a freezing mixture of ice and salt. This condenses the vapour in B and lowers the pressure of vapour in the tube. Water in A evaporates to restore the pressure ; more vapour is condensed at B and more water evaporates in A. This process goes on, and the evaporation lowers the temperature of the water in A until it finally freezes. It is advisable to wrap the bulb A in flannel or other poor conductor, otherwise heat is absorbed from the air and the water takes a very long time to freeze, and may even fail to do so. It will be observed that the process is precisely similar to that described

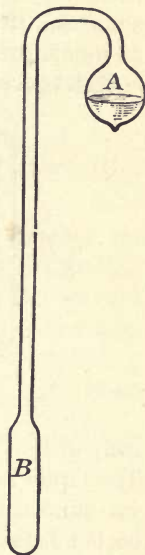


FIG. 75.

<sup>1</sup> If the under side of the watch-glass is wet, the experiment seldom succeeds.

in the previous paragraph, except that the vapour is removed by condensation instead of by sulphuric acid.

The danger of standing about in wet clothes is due to the great absorption of heat on evaporation; anything that increases the evaporation, such as a wind which carries away the vapour as it forms, increases the danger. Compare the advice to a benighted party given in the Badminton volume on Mountaineering: "The cold due to evaporation is much more to be dreaded than a low temperature. If any man then has anything that is dry, let him put it on. A Scotch shepherd, if his plaid is partly wet through and he is caught at night, turns his plaid with the wet side in."<sup>1</sup>

**Refrigerating Machines.**—The cooling due to rapid

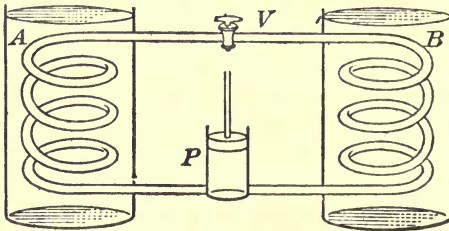


FIG. 76.

evaporation is made use of in many refrigerating machines. The liquid is made to evaporate rapidly in a spiral metal pipe surrounded by a vessel containing strong brine, which can be cooled below  $0^{\circ}\text{C}$ . without freezing. The substances to be cooled are placed in the brine, e.g. vessels containing water can be put in, and the water will be frozen to a solid block of ice.

It is usual to employ either ammonia gas or carbon dioxide liquefied under pressure as the evaporating liquid, and the process is rendered continuous by an arrangement illustrated diagrammatically in Fig. 76.

<sup>1</sup> The present writer is unacquainted with the habits of Scotch shepherds, but the principle is sound, and he has often applied it.

The gas is compressed by the pump P and liquefies in the pipe A, which is kept cool by circulating water. The liquid is admitted through the regulating valve V into the spiral B. It evaporates there, the pump drawing off the vapour and re-delivering it to A. The process is thus continuous, evaporation constantly going on in B, which forms the refrigerating part.

For most purposes ammonia is the most convenient substance. Carbon dioxide involves much higher pressures; it has the advantage, however, that the apparatus can be smaller, and if the gas should escape by an accidental burst, carbon dioxide is less injurious than ammonia. Refrigerating machines are examples of reversed heat engines or "heat pumps" (see Chapter XXI).

### Change of State as a Means of Measuring Quantities of Heat.

Instead of measuring a quantity of heat by finding the change in temperature of a known mass of water, we can make the heat melt ice or vaporize water, and if the amount of ice melted or water vaporized be measured, and the latent heat is known, the amount of heat is readily calculated.

**Ice Calorimeters.**—The most satisfactory of these is Bunsen's (Fig. 77). The amount of ice melted is determined indirectly, by making use of the change in volume when ice turns to water. The apparatus consists of a glass bulb Q, into the top of which is fused a tube P, and which terminates in a tube. This tube is provided with a collar S into which a narrow tube R fits. The upper part of Q contains water,

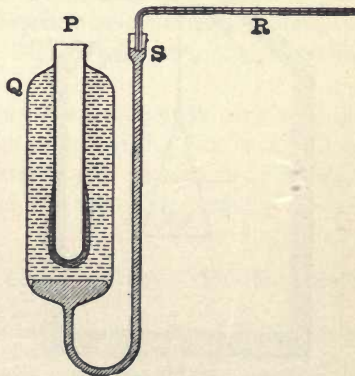


FIG. 77.

carefully freed from air, while the lower part and the tube S contain mercury. Some of the water in Q is frozen by drawing alcohol, cooled in a freezing mixture, through P. In this way a cap of ice is formed round P. Some distilled water is placed in P, and then the whole apparatus is surrounded by melting ice or snow and left for a long time so that it takes up a temperature of  $0^{\circ}\text{C}$ . The substance whose specific heat is to be measured is heated to a known temperature, e.g. in a steam heater, and dropped into P. It cools down to  $0^{\circ}\text{C}$ . and melts some of the ice. The contraction in volume causes the mercury in R to move. The distance moved is measured and the contraction in volume is thus found if the bore of the tube R is known. From this the amount of ice melted is known, and so the amount of heat given up by the solid in cooling to  $0^{\circ}\text{C}$ . is found. In practice the apparatus

is usually calibrated directly by measuring the movement of the mercury in C when a known mass of hot water at a known temperature is placed in D.

It will be observed that there is no correction for the water equivalent of the calorimeter since this starts and ends at the same temperature; nor is there any cooling correction. The apparatus is by no means easy to use, but it gives good results and is well adapted for finding the specific heats of substances when only a small quantity is available.

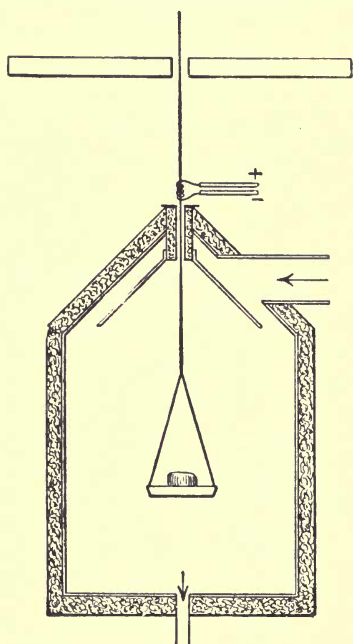


FIG. 78.

**Joly's Steam Calorimeter.**—In this apparatus



(Fig. 78) the idea is to place the substance in a pan suspended from one arm of a balance and enclosed in a chamber into which steam can be passed.

The substance is placed in the pan and left for some time so as to take up the temperature of the chamber, which is given by a thermometer. Steam is then passed through the apparatus as shown by the arrow. Some of this steam condenses on the substance, raising its temperature; as soon as its temperature reaches the boiling-point no more steam condenses and the weight becomes constant. The increase in weight gives the weight of steam condensed.<sup>1</sup> The substance rests on a network of threads so as not to touch the pan. Otherwise so much steam will condense on the lower side of the pan that a little water may drop and be lost. An alternative is to have a catch-water attached to the underside of the pan.

Now, if  $w$  grams of steam were condensed,  $537 \times w$  calories have been used in raising the temperature of the substance and pan from the initial temperature of the chamber to the boiling-point of water. A preliminary experiment is made to find out the thermal capacity of the pan and supports, the weight of steam condensed being found when there is no substance in the pan.

A spiral of platinum wire made red hot by an electric current prevents steam condensing and forming a drop of water where the supporting wire passes out, which would interfere with the weighing.

The method is quick and very accurate; it is very suitable for dealing with small quantities of material. Solids or liquids which would be affected by steam can be sealed up in thin glass vessels; a correction for the thermal capacity of this vessel must be made.

### Specific Heats at Low Temperatures.—The substance

<sup>1</sup> A correction is necessary, because there is an apparent change in weight owing to the first weight of the substance being taken in air, and the second in steam, which is less dense than air and consequently exerts a smaller upthrust on the body.

is first brought to a definite temperature, say that of liquid nitrogen at atmospheric pressure, and then dropped into liquid hydrogen, which is at a temperature much lower than that of liquid nitrogen. The amount of hydrogen evaporated is found by measuring the volume of the gas given off, and hence the heat given up to it is calculated. The liquid hydrogen vessel is surrounded by a jacket filled with liquid hydrogen also to prevent the evaporation of hydrogen in the vessel due to absorption of heat from its surroundings.

## CHAPTER XI

### HYGROMETRY

Evaporation is constantly taking place from the surface of the sea and inland water, and a notable amount takes place from the surface of the leaves of trees and plants ; on the other hand, water returns to earth in the form of rain, dew, etc. Thus the air always contains more or less water vapour as one of its constituents ; the amount varies according to circumstances. A knowledge of the amount of water vapour in the air is of importance in meteorology, and the measurement of it is termed hygrometry.

The presence of this vapour is easily demonstrated. If a glass flask or a metal vessel is filled with water cooled by a little ice, a film of moisture is soon formed on the outside. A piece of fused calcium chloride exposed to the air absorbs moisture and becomes pasty and finally liquid, forming a solution of calcium chloride in water. The same effect may be shown in another way by drawing air through a U-tube containing fused calcium chloride or glass beads moistened with strong sulphuric acid. If the tube be weighed before and after, it will be found to have gained in weight owing to absorbed moisture.

We saw in Chapter X that at any particular temperature a given space can only contain a certain amount of water vapour whether air is present or not ; if there were more vapour the pressure would be above the saturation pressure and some vapour would condense.<sup>1</sup> We also saw that the amount of water vapour required to saturate a given volume

<sup>1</sup> But see page 183 on the necessity for some nucleus on which to condense.

is much greater at high temperatures than at low ; thus warm air can contain a greater quantity of aqueous vapour per unit volume than can cold air. As a general rule the amount of aqueous vapour in the air is less than that required to saturate it, and the *Relative Humidity* of the air is defined as—

Amount of aqueous vapour per unit volume

---

Amount of aqueous vapour per unit volume required to saturate the air at the same temperature.

**Formation of Clouds and Mist.**—If a mass of air, which contains less vapour than is required to saturate it, is quickly cooled, the amount of vapour which it contains may exceed that required to saturate it at the lower temperature, and condensation takes place throughout the mass. A large number of small drops are formed which constitute a cloud or mist. There are two very common ways in which cooling may take place :—

(1) A current of warm air carrying a good deal of aqueous vapour may meet a colder current, and condensation takes place where they meet. The fog-banks off the coast of Newfoundland are usually quoted as examples of this.

(2) A much more general effect is the case of a mass of air passing rapidly up into a region of lower pressure, e.g. a wind blowing against mountain sides and deflected upwards. The mass of air expands, and when a gas expands it does work (see Chapter XIX) involving absorption of heat. The cooling may be sufficient to cause condensation.

**Formation of Dew.**—The formation of dew is a case of local condensation. If we have a cold object, the air in contact with it will be cooled, and may reach a temperature at which the vapour in it is sufficient to saturate it, and it will begin to deposit moisture on the object. The effect will take place much more readily if the object is on or near the ground ; if it is not, the air as it cools, becoming denser, will sink before it has reached the saturation-point and more air will take its place. In the same way the effect will be hindered if the air is not still, since a given portion of air will not remain in contact with the object.



Now, on a clear night radiation takes place freely from the surface of the earth, so that objects on the earth become very cold.

If the sky is cloudy, the clouds act as a screen, sending back a good deal of the radiation. Thus dew forms more readily on a clear night than on a cloudy one. The best conditions for the formation of dew are provided when a hot day is followed by a clear still night. During the day evaporation into the atmosphere takes place readily, since the air can contain a great deal of aqueous vapour before reaching its saturation-point; while the clear night favours radiation.

It may be noted that the heavy deposit of dew on grass and the leaves of plants is not wholly produced by deposition from the atmosphere; we have seen that the leaves give off water, and if the air in contact with them is already cooled to the saturation-point this water cannot pass off as vapour, but appears as liquid.

**Hoar Frost.**—If the objects are at a temperature below freezing-point any condensation will be direct from vapour to solid. Thus, hoar frost is not frozen dew, but ice formed directly from vapour.

**Condition of the Air. Relative Humidity.**—In meteorological work a knowledge of the condition of the air is of value; if the air is nearly saturated very slight cooling will bring about condensation. It will be seen that what we want to know is not so much the actual amount of vapour in the air as the relative humidity. This is also a guide as to the general feeling of the air; if the relative humidity is low, evaporation readily takes place into the air, which in consequence feels "dry," while if the relative humidity is high—i.e. the air is nearly saturated—very little evaporation can take place and the air feels damp. It may often happen that the air on a hot summer's day contains much more vapour than on a cold damp day in winter, but since the amount required to saturate the hot air is so great, the relative humidity is lower and the air feels dry.



**Measurement of Relative Humidity.**—We have defined relative humidity as—

$$\frac{\text{Amount of water vapour per unit volume}}{\text{Amount of water vapour per unit volume required to saturate the air at the same temperature.}}$$

Amount of water vapour per unit volume required to saturate the air at the same temperature.

Instead of expressing the amount of water vapour as so many grams per unit volume it is often more convenient to express it in terms of the partial pressure it exerts.

**Properties of a Mixture of Gases and Vapours.—Partial Pressures.**—The experiments of Dalton, confirmed by the much more elaborate work of Regnault, showed that if we have a space occupied by a mixture of gases and vapours, which do not have any chemical action on one another, the total pressure is equal to the sum of the pressure which each constituent would exert by itself if it occupied the whole volume. For example, if we had 1 litre of nitrogen, measured at 500 mm. of mercury, 1 litre of oxygen measured at 250 mm., and 1 litre of water vapour measured at 10 mm., and put them all into a 1-litre vessel, the pressure of the mixture would be 760 mm.<sup>1</sup>

It is easy to see that this is so, if each constituent obeys Boyle's Law. Thus we may regard each constituent as diffused through the whole volume, and contributing to the total pressure a partial pressure equal to that which it would exert if the other constituents were not there. Regnault also made experiments which showed that although water vapour does not obey the laws of Boyle and Charles so closely as a gas like nitrogen or oxygen, the departure is quite small for moderate pressures except near saturation point. Even here later work shows that the deviation at moderate temperatures is not more than about 1 or 2 per cent. In

<sup>1</sup> This is not strictly true, and experiments made at high pressures show considerable deviations from this law. This is to be expected when the molecules are closely packed (see Chapter XVIII). At pressures of the sort met with in the atmosphere the law is sufficiently near the truth for all practical purposes and is assumed to be true in meteorological calculations.

Hygrometry, therefore, it is usually assumed that water vapour obeys these laws up to the saturation point.

Relative humidity is therefore also defined as—

Pressure of aqueous vapour actually present

Saturation pressure of aqueous vapour at the same temperature.

**Determination of Relative Humidity by the Dew-point Method.**—If a portion of the air in an open space be cooled, the cooled air contracts but the pressure remains constant, equal to the atmospheric. The pressure of the water vapour in it also remains constant, since the vapour contracts in the same proportion as the air. A stage is reached, however, at which the temperature is such that the pressure of the water vapour corresponds to the saturation pressure; if the cooling is continued condensation will take place and the pressure of the vapour will fall. This temperature, when condensation can just take place, is called the *dew-point*, and it will be seen that the pressure in the air before cooling is equal to the saturation pressure at the temperature of the dew-point.

For example, if the dew-point were found to be  $8^{\circ}\text{C}$ ., we see from the tables that the saturation pressure at this temperature is 8.6 mm. Then we can say that the pressure of vapour in the air before cooling was 8.6 mm.

**Daniell's Hygrometer.**—This instrument, the oldest form of hygrometer, is sometimes used, but is now recognized as unreliable.

**Dines' Hygrometer.**—A very simple hygrometer is that due to Dines (Fig. 79). A reservoir A contains water cooled by ice. It communicates with a thin metal box B closed at the top with a thin sheet of black glass C. The thermometer D has its bulb just under the glass plate, and its stem in a groove in the wooden block which supports the parts of the apparatus. The box B is full of water at room temperature. By opening the tap T ice-cold water from the reservoir is allowed to flow into B which is provided with an outlet E. Thus the glass

plate is gradually cooled, until a deposit of dew is seen ; the temperature is noted, and the flow of cold water stopped. After a time the dew disappears as the plate gradually becomes warmer, and the temperature at which this happens is noted.

The mean of these two temperatures, if they do not differ much, is taken as the dew-point. If they do differ much, the experiment must be repeated and the cooling carried out more slowly, so that the two temperatures do not differ by more than one or two tenths of a degree.

It is important that the observer should not be too near,

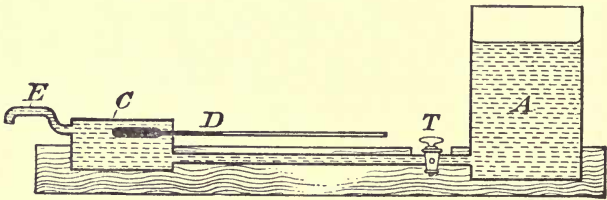


FIG. 79.

otherwise his breath will affect the humidity of the air. The thermometer can be read by a telescope and inclined mirror ; observation of dew is facilitated by viewing the black glass by means of a beam of light reflected from the surface. Failing these precautions a large sheet of glass must be interposed between the observer and the instrument.

**Regnault's Hygrometer.**—Regnault's hygrometer is very satisfactory. The apparatus consists of a glass tube A (Fig. 80), to the lower end of which is cemented a capsule made of thin silver, highly polished on the outside. The glass tube is closed at the top by a cork through which passes a tube reaching nearly to the bottom of the apparatus. A side tube communicates through the tubular support with a long rubber tube connected to an aspirator. Ether is placed in the apparatus, and air is drawn through it by means of the aspirator. By this means the silver capsule is cooled, and

the temperature at which dew is deposited is noted. The flow of air is stopped and the temperature at which dew disappears is noted.

The thermometer is read by means of a telescope, and the rate of cooling can be completely controlled by means of the aspirator, which is some distance off; the observer therefore need not come near the apparatus. The bubbling of the air through the ether acts as a stirrer, so that the temperature of the whole of the ether is given by the thermometer.

It is not very easy to see the deposit of dew, and observation is facilitated by having a similar tube B for comparison. Air is not drawn through this tube.

The two forms of hygrometers described only give good results if the air is still; if there is a draught the formation of dew is prevented unless the temperature is much below the true dew-point.

**The Wet and Dry Bulb Hygrometer.**—A form of hygrometer which is very much in use is the wet and dry bulb hygrometer (known in this country as Mason's hygrometer). Two thermometers, of the same shape and size, are mounted side by side, but the bulb of one of them is enclosed in a piece of muslin which is kept moist by means of pieces of cotton wick dipping into the small vessel of water <sup>1</sup> (Fig. 81).

<sup>1</sup> Details of the most satisfactory arrangement are given in *The Observers' Handbook*, published by the Meteorological Office, which also contains Glaisher's Tables.

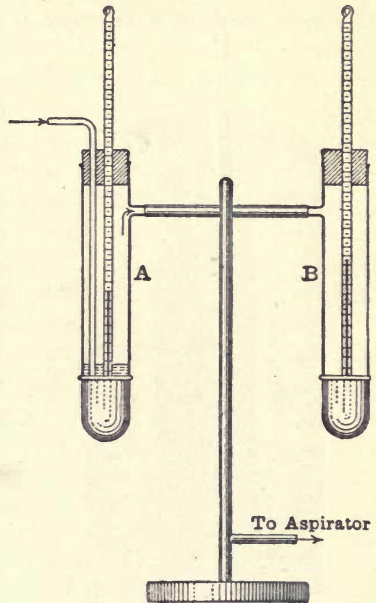


FIG. 80.

As evaporation takes place from the muslin, heat is absorbed, and the wet bulb thermometer indicates a lower temperature than the other. The difference in temperature depends on the rate of evaporation, which again depends on the relative humidity of the atmosphere; if the air is saturated, the two thermometers give the same reading. Tables have been

drawn up, from which the dew-point may be obtained if the dry bulb reading and the difference of the readings of the wet and dry bulb are known. Since the rate of evaporation would be increased by motion of the air, the instrument is usually placed in a Stevenson screen, which is essentially a chamber with double louvre sides, i.e. sides arranged like a double row of Venetian blinds.

The instrument is quickly and easily read, but cannot be regarded as accurate. The readings are appreciably influenced by the surroundings; and it does not seem possible to deduce a relation between the readings and the actual pressure of water vapour in

the air. The only reasonable method appears to be to compare the readings of the instrument with those of one of the other types.

*Modern Forms.*—In order to avoid the uncertainties caused by air currents, modern hygrometers of the wet and dry bulb type are usually provided with an arrangement by which the air is drawn over the bulbs at a known constant rate.

A type of dew-point instrument which is reliable has been

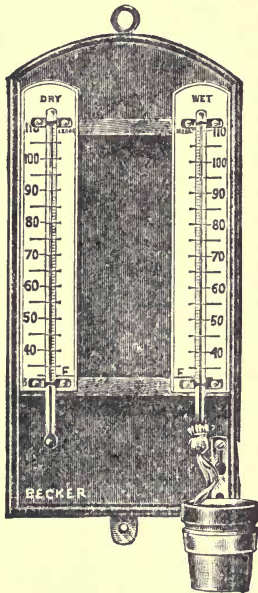


FIG. 81.



designed by M. Crova. Instead of letting the dew be deposited on the outside of a cooled vessel, Crova has a thin brass tube, closed except for an inlet and outlet, which is gradually cooled down from the outside while air is slowly drawn through it. When the tube reaches a low enough temperature, dew is deposited on the inside and is made visible by an ingenious optical arrangement. For particulars of this instrument reference may be made to Preston's *Heat*; others are described in makers' lists such as those of Negretti and Zambra.

Glaisher's tables, used by the Meteorological Office, are based on a long series of comparisons with a Daniell hygrometer; we have already seen that this is not a trustworthy instrument. The wet and dry bulb hygrometer must therefore be regarded as an extremely convenient instrument for giving a rough value of the humidity of the air at any time.<sup>1</sup> Moreover, since it can be enclosed in a Stevenson screen, it is suitable for use out of doors, under conditions where Dines' and Regnault's could not be used. It is therefore the instrument used at meteorological stations.

**The Chemical Hygrometer.**—The chemical hygrometer is simply an arrangement in which a known volume of air is drawn through drying tubes, and the weight of aqueous vapour is determined directly. It is very accurate but somewhat tedious, and it should be noted that it does not give the state of the air at some particular moment, but the average condition during the time of the experiment.

Fig. 82 shows the arrangement. A and B are drying tubes containing pumice moistened with strong sulphuric acid; these are weighed before and after the experiment.<sup>2</sup> P is a small tube containing phosphorus pentoxide<sup>3</sup>; it is weighed before and after and is used to see that A and B are really absorbing all the water vapour. P should not change in weight; if it does the

<sup>1</sup> The compilation of more reliable tables for the wet and dry bulb hygrometer is at present receiving attention.

<sup>2</sup> During the weighing and at all times except while the air is being drawn through them, the side tubes of the U-tubes are closed with glass plugs.

<sup>3</sup> P is known as a "policeman," since it is there to see that A and B perform their office.

experiment must be done again. Air is drawn through by means of the aspirator *E*, and the drying tube *C* is used to prevent any aqueous vapour diffusing back from *E* into the weighed tubes. The syphon tube is filled before connecting up the drying tubes, and is then closed by the screw clip *D*. When the tubes are connected *D* is partially opened and the air is slowly drawn through; several litres are allowed to pass, the volume of the air which has come into the aspirator being determined by the volume of water which flows out.<sup>1</sup>

If an accuracy of 1 or 2 per cent. is sufficient, the relative

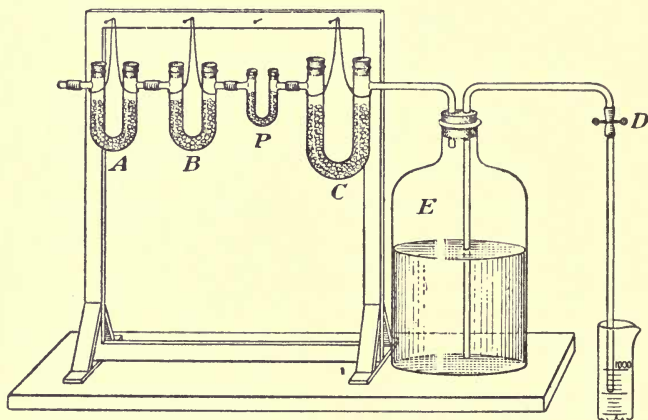


FIG. 82.

humidity of the air can be obtained by a very simple calculation. Let  $w$  be the weight of water vapour, and  $V$  litres the volume of air as measured by the amount of water which flowed out of the aspirator. If  $T_w$  is the temperature of the air in the aspirator, determined by taking the temperature of the water, and  $T_A$  the temperature of the air outside we can assume that the volume of the air which passed through the drying tubes is  $V \cdot \frac{273 + T_A}{273 + T_w}$

<sup>1</sup> Care must be taken to start and finish at atmospheric pressure; at the finish the measuring cylinder is raised until the level of the water in it is the same as that in the aspirator, and *D* is then closed. At the beginning of the experiment a test should be made to see that all connections are airtight; this can be done by seeing that the insertion of a glass plug at *F* causes the flow of water to stop.

we neglect the fact that the air in the aspirator is saturated with aqueous vapour at  $T_w$ , while that outside contains an unknown amount. The neglect of this fact simplifies the calculation, but may introduce an error of 1 or 2 per cent. (see p. 182). Then  $w$  grs. is the weight of aqueous vapour in  $V \cdot \frac{273 + T_A}{273 + T_w}$  litres.

The weight of aqueous vapour which would saturate this volume of air at  $T_A$ ° C. can be obtained directly from Regnault's tables,<sup>1</sup> or by repeating the experiment with saturated air, which may be done by drawing the air through tubes containing pieces of glass tube moistened with water before it comes to the drying tubes.

If  $W$  is the weight of water which saturates  $V \cdot \frac{273 + T_A}{273 + T_w}$  litres of air at  $T_A$ , the relative humidity of the original air is simply  $\frac{w}{W}$ .

Although the above method is good enough for many purposes, the following method of calculating the pressure of the aqueous vapour from the results of the experiment without making simplifying assumptions should be carefully considered, not only for its own sake but because it illustrates the methods adopted in many operations with gases.

Consider the air which has passed through the tubes. It starts at a temperature  $T_A$ ° C., and contains aqueous vapour at a pressure  $f$  which we are trying to find. It gives up its moisture and comes into the aspirator where it takes up the temperature of the water  $T_w$ ° C. and becomes saturated with aqueous vapour at this temperature. Its volume is then  $V$  litres (which is measured), and we require to know its original volume  $V'$ . Let  $H$  be the barometric pressure, and  $p$  the saturation pressure of aqueous vapour at  $T_w$ °. In the aspirator, the partial pressure of the air is  $H - p$ , the remainder of the total pressure,  $p$ , being due to vapour. Before it came in, the partial pressure was  $H - f$ . Thus  $V'$  litres of air at  $T_A$ ° and  $H - f$  mm. have become  $V$  litres at  $T_w$ ° and  $H - p$  mm. Thus by the ordinary Boyle and Charles Laws we have

$$V' = V \cdot \frac{H - p}{H - f} \cdot \frac{273 + T_A}{273 + T_w} \cdot \dots \dots \dots (1)$$

<sup>1</sup> See Kaye and Laby's *Tables of Physical and Chemical Constants*, Third Edition, page 39. Published by Longmans, Green & Co.

As we do not know  $f$ , we cannot determine  $V'$  by this equation alone.

But we have seen on page 174 that at temperatures and pressures such as we are now considering, water vapour may be regarded as obeying the gas laws, and we can calculate its density at any pressure just as we should in the case of a gas. Now it is found that the density of water vapour is  $\cdot 622$  times that of air at the same temperature and pressure.<sup>1</sup>

Now 1 litre of dry air at  $0^\circ \text{C}$ . and 760 mm. weighs 1.293 gms.

$\therefore$  1 litre of dry air at  $T_A^\circ$  and  $f$  mm. weighs—

$$1.293 \times \frac{f}{760} \times \frac{273}{273 + T_A}$$

$\therefore$  1 litre of water vapour at  $T_A^\circ$  and  $f$  mm. would weigh—

$$0.622 \times 1.293 \times \frac{f}{760} \times \frac{273}{273 + T_A} \text{ gm.}$$

But the actual weight of the water vapour in  $V'$  litres was  $w$  grams.

$$\therefore w = 0.622 \times 1.293 \times \frac{f}{760} \times \frac{273}{273 + T_A} \times V'$$

$= 0.8 \times \frac{f}{760} \times \frac{273}{273 + T_A} \times V'$ . Substitute for  $V'$  by means of (1) and we have

$$\begin{aligned} w &= 0.8 \times \frac{f}{760} \times \frac{273}{273 + T_A} \times \frac{273 + T_A}{273 + T_w} \times \frac{H-p}{H-f} \times V \\ &= 0.8 \times \frac{f}{760} \times \frac{273}{273 + T_w} \times \frac{H-p}{H-f} \times V \end{aligned}$$

which gives the value of  $f$ , since  $H$ ,  $w$ ,  $V$ ,  $T_w$  and  $p$  are known.

It will now be seen that the simplifying assumption mentioned above, was the neglect of the factor  $\frac{H-p}{H-f}$ ; in most cases  $f$  is not likely to differ from  $p$  by as much as 12 mm., which is less than 2 per cent. of 760 mm.

**Rate of Fall of Clouds and Mists.**—When a drop of water is falling through air, it experiences a resistance which increases with the velocity. When the velocity becomes so great that the

<sup>1</sup> This is an experimental result due to Regnault. It may be noticed that since the Molecular Weight of  $\text{H}_2\text{O}$  is about 18, we should expect the vapour density with respect to air to be about  $\frac{9}{14.4} = \cdot 625$ .



resistance is equal to the weight of the drop, no further increase takes place, and the drop falls with a uniform velocity called the limiting velocity. This limiting velocity is proportional to the square of the radius of the drop; <sup>1</sup> for a drop of radius .01 mm. the limiting velocity is something like 1 cm. per sec. A dense fog is made up of a large number of very small drops; so also is the sort of cloud seen at fairly high elevation. The rate of fall of these is excessively slow. A so-called Scotch mist is made up of larger drops, and can be seen to have an appreciable rate of fall. The rate of fall of large rain drops (e.g. a thunder shower) is visibly greater than that of small.

#### Vapour Pressure at a Curved Surface—Condensation Nuclei.

—The saturation pressure at a curved surface differs from that at a flat; for a convex surface it is greater, and at a concave it is less. The difference increases with the curvature of the surface. Thus a very small drop of water, where the curvature of the surface is great, would tend to evaporate in a space where the pressure of the vapour was the ordinary saturation pressure. This accounts for the fact, demonstrated by Aitken and investigated in detail by C. T. R. Wilson, that in air which is free from small dust particles it is difficult for a cloud to form, even though the pressure of vapour is greater than the saturation pressure. Wilson, by suddenly cooling air saturated with aqueous vapour, showed that if the air were carefully freed from dust, a degree of supersaturation of something like eight times the normal was required to form a cloud, although a few large drops were formed if the supersaturation was about four times the normal. With ordinary air a dense cloud is formed with a smaller degree of supersaturation. The function of the dust particles is to provide nuclei for the drops to form on; otherwise it is difficult to start a drop since its radius must be indefinitely small to begin with, and therefore its curvature indefinitely great. For this reason the formation of dense fogs (i.e. fogs where there are large numbers of very small drops) is much facilitated by the presence of particles in the air; towns with a smoky atmosphere like Sheffield

<sup>1</sup> Stokes showed that the resistance at any velocity is given by  $6\pi r\mu u$  where  $\mu$  is the coefficient of viscosity of the air. If  $u$  is the limiting velocity,  $6\pi r\mu u$  must equal the weight of the drop  $\frac{4}{3}\pi r^3\rho g$  (neglecting buoyancy of air). Thus  $6\pi r\mu u = \frac{4}{3}\pi r^3\rho g$  or  $u = \frac{2}{9} \cdot \frac{\rho g}{\mu} \cdot r^2$ .



are subject to dense fogs, and a generation or two ago London used to provide very fair specimens. Delayed boiling is also an example of the influence of curved surfaces on vapour pressure. Consider a small bubble of vapour in the liquid. Since the inside surface is concave, the pressure of vapour will not be equal to the atmospheric unless the temperature is above the normal boiling point. Thus it is difficult for the bubble to form unless it has something to form on. The influence of surface tension also comes in.

In the absence of anything on which to form the temperature may rise considerably above the boiling point, but if a bubble does form it grows with great violence, since the pressure increases with the size of the drop owing to diminished curvature.

**Lord Kelvin's proof that the vapour pressure depends on the curvature of the surface.**

Let Fig. 83 represent a dish of water in which is placed a narrow tube open at each end. Let the whole be placed under an exhausted bell jar, so that the space inside contains only vapour.

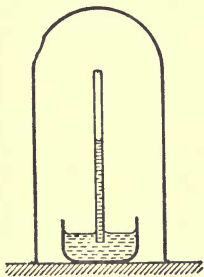


FIG. 83.

Owing to surface tension, the water rises to a height  $h$  in the tube,  $h$  being inversely proportional to the bore of the tube. The surface of the water in the tube will be concave. Now the pressure of the vapour in contact with the water in the dish will be  $p$ , where  $p$  is the saturation pressure.

Since, however, the vapour has weight like any other fluid, the pressure at a height  $h$  in the vapour will be less than  $p$  by an amount equal to the pressure due to the weight of a column of vapour of height  $h$ . The surface of the liquid in the tube is therefore in contact with the vapour at a lower pressure than  $p$ ; if then curvature makes no difference to the vapour pressure, water would tend to evaporate until the pressure in its neighbourhood became  $p$ . But this would make the pressure at the surface of the dish greater than  $p$  and condensation would take place. Thus water would continually evaporate from the tube and more would rise from the dish to maintain the height  $h$ . Thus we should have continuous circulation, and "perpetual motion." As this does not occur the water in the tube must be

in equilibrium with the vapour at the lower pressure. In the case of a liquid with a convex surface, e.g. mercury, the liquid in the tube would be below that in the dish, and the same argument would show that the vapour pressure at the convex surface was greater than that at the flat. To obtain a quantitative relation, let  $\sigma$  = density of the vapour. Then the difference between the pressure at the two levels is  $hg\sigma$  dynes per sq. cm.<sup>1</sup>

Now if  $T$  is the surface tension of the liquid,  $r$  the radius of the tube at the top of the liquid column, and  $\rho$  the density of the liquid, then if the angle of contact is  $0^\circ$   $\pi r^2 \rho h g = 2\pi r T$ <sup>2</sup>

$$\text{or } h = \frac{2T}{\rho g r}.$$

If we regard the surface of the water as approximately semi-circular,  $r$  is also the radius of curvature of the surface.

Thus the difference of pressure at the two surfaces is

$$hg\sigma = g\sigma \cdot \frac{2T}{\rho r g} = 2T \cdot \frac{\sigma}{\rho} \cdot \frac{1}{r}.$$

<sup>1</sup> Strictly speaking  $\sigma$  would be greater at the bottom than the top owing to the compressibility of the vapour.

<sup>2</sup> Strictly  $\pi r^2 g h (\rho - \sigma)$ , since pressure on the top of the column is  $hg\sigma$  less than on the surface of the liquid.

## CHAPTER XII

### TRANSMISSION OF HEAT

#### CONDUCTION

In the two preceding chapters we have seen something of the nature of heat and its relation to work ; we have now to consider the ways in which heat can pass from one place to another, and the conditions which govern its transmission.

Let us suppose we have a thick metal vessel (Fig. 84), containing water, and we place it on the flame of a bunsen burner. Consider, first, what happens in the metal. The outside portion of the bottom, which is in contact with the flame, becomes hotter ; the layer next to this receives heat from it, and so on until the inside of the metal in contact with the water becomes heated and begins to communicate heat to the water. At this stage there is a progressive fall of temperature from the outside portion in contact with the flame to the inside, which is just warmer than the water. The metal continues to rise in temperature, but the rise is soon checked ; the heat communicated to the outer layer is carried off as it is supplied.<sup>1</sup>

At this stage it is still true that the side of the metal in contact with the flame is hotter than the side in contact with the water.

Heat is passing into the water through the metal ; it is said to be transmitted by *conduction*. Each portion of the

<sup>1</sup> As, however, the water gradually becomes warmer the temperature of the metal rises gradually also until the boiling-point is reached, when the temperature of each part of the metal remains stationary. Heat continues to be supplied to the water and is used up in turning water to steam (see page 195).

metal along the direction of flow receives heat from a part at a higher temperature and passes it on to one at a lower.

The distribution of the heat to the different parts of the water is chiefly brought about by another method. The water heated by the metal expands, and, becoming less dense, rises to the surface, as indicated by the arrows, while colder water flows in to take its place and become heated in turn. A circulation is started, which can be made evident by putting in a few pieces of damp sawdust or bran. Thus the heat travels to different parts of the vessel by the actual movement of portions of the water conveying heat with them. This process of distribution of heat is therefore spoken of as *convection*.

There is, however, a third method by which heat can be transmitted from one place to another; this method is altogether different from those we have considered. If we stand in the sunshine, we are conscious of a feeling of warmth; it is not a case of the air being warmed and passing on heat to us, for if a cloud passes between us and the sun, we are immediately aware that the heating effect has stopped. Moreover, the effect is very noticeable even when the temperature of the air is below freezing-point, e.g., at high elevations in Switzerland or Norway one can often sit comfortably in the sunshine with one's coat off although the snow is hard and the air below freezing-point.

This is a case of the transmission of heat by *radiation*, and the essential point is that the transmission takes place without raising the temperature of the intervening medium. This essential point is well illustrated by a modification of the well-known effect of a lens or "burning glass," by which the sun's radiation is made to light a pipe or set fire to paper;

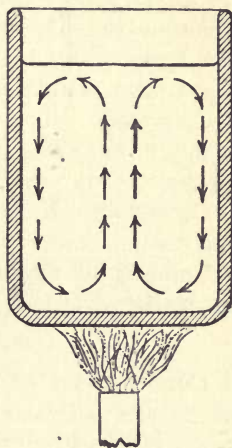


FIG. 84.

a lens of ice is made by means of a mould, and the effect of setting fire to paper can still be produced, although the transmission must have taken place through a medium at a temperature not greater than  $0^{\circ}\text{C}$ .

A large amount of the heat received when one stands before a fire is transmitted by radiation; very little by conduction through the air.

Thus there are three ways in which heat can be transmitted from one place to another:—

*Radiation.*—The transmission takes place without raising the temperature of the intervening medium. It can take place most readily across a vacuum.

*Conduction.*—The temperature of the intervening medium is raised, but there is no appreciable<sup>1</sup> movement of portions of the medium along the direction of flow of heat.

*Convection.*—Heat is conveyed by appreciable portions of the medium moving along the direction of the flow of heat.

These three methods must now be considered separately in greater detail.

### CONDUCTION

**Conductivity of Solids.**—It is easy to show that some solids conduct heat much more readily than others. For example, if a silver teaspoon or a short length of thick copper wire has one end immersed in a vessel of boiling water, the other end rapidly becomes too hot to hold; under the same conditions a glass rod or tube can be held for any length of time without becoming particularly warm. When glass tubing is being worked in the blow-pipe flame it is possible to take hold of a part of the tube only an inch or two from the flame.

We therefore say that silver and copper are good conductors of heat, while glass is a bad conductor. The thermal conductivity of a substance has, however, a precise meaning, and can be expressed as a number.

<sup>1</sup> The word "appreciable" is put in so as not to exclude molecular movement.



**Definition of the Thermal Conductivity of a Substance.**—Consider a plate of the material of thickness  $t$ . Let one face of the plate be maintained at a temperature  $\theta_1$ , and the opposite face at  $\theta_2$ . Then heat will be flowing through the plate, and experiment shows that for any given material, the quantity of heat flowing through the plate per second is proportional to the temperature difference  $\theta_1 - \theta_2$ , and inversely proportional to  $t$ . It is also, of course, proportional to the area of the plate, and depends on the material.

The *thermal conductivity of the material* is defined as the amount of heat per second which flows across unit area of a plate of unit thickness when the difference of temperature of the opposite faces is maintained at one degree. Thus if  $K$  were the thermal conductivity of the material, the amount of heat flowing per second across unit area would be  $K \cdot \frac{\theta_1 - \theta_2}{t}$ .

We may call  $\frac{\theta_1 - \theta_2}{t}$  the temperature gradient along the direction of the flow of heat, and we can then get a shorter and more general definition of  $K$  as follows:—

The thermal conductivity of a substance is the amount of heat flowing per second across unit area perpendicular to the flow when the temperature gradient along the direction of flow is one degree per unit length.

**Determination of the Thermal Conductivity of a Metal by Searle's Apparatus.**—A solid bar of the metal (Fig. 85), about 5 cm. diam. and 20 cm. long, is fitted at one end to a circular chamber A, through which steam can be passed. Near the other end a coil of thin copper tubing, B, is soldered to the bar. The ends of this tubing are connected to copper cups. Cold water circulates through B. The bar with its fittings is surrounded by thick layers of felt packed in a wooden box, made in two halves; in the figure one half is removed. Steam circulates through A, and the rate of flow of the cold water through B is kept steady. This water receives heat from the bar, and the amount of heat received per second is determined by finding the weight of water

flowing in a given time and reading the difference between the temperature of the water when entering and leaving B. The thick felt packing prevents any appreciable loss of heat from the bar except that which is given to the circulating water; a steady state is therefore reached in which the flow of heat down the bar is equal to that received by the water

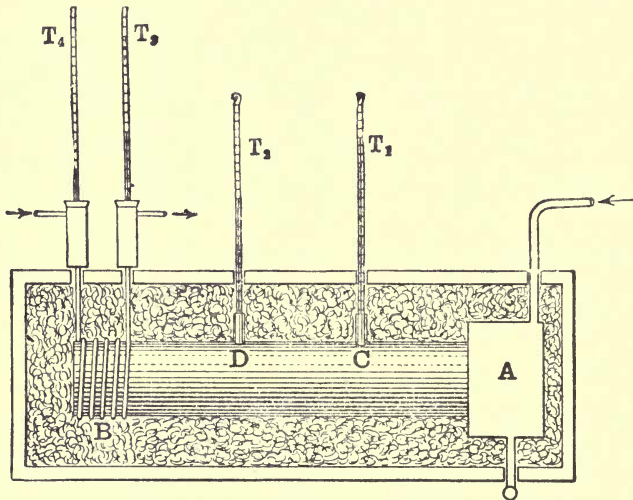


FIG. 85.

When this state is reached there is a temperature gradient down the bar, and since heat enters the bar at the end in contact with the steam chamber and leaves it at B and nowhere else, it follows that the amount of heat which flows per second across any section between B and A is the same.

The temperature gradient can be measured at any convenient place, and is determined by the difference between the readings of the thermometers  $T_1$  and  $T_2$  placed in copper tubes C and D brazed into the bar at a known distance apart.<sup>1</sup>

<sup>1</sup> It would not be at all accurate to assume that the hot end of the bar was at  $100^\circ \text{C}$ . and the cold end at the mean temperature of the water. In the case of a good conductor like copper the temperature

In carrying out an experiment it is necessary to wait until the readings of all four thermometers are constant. The following figures will explain the method of calculation:—

Reading of $T_3$	23° C.
„ „ $T_4$	14.7° C.
Rate of flow of water	205 gm. per minute = 3.417 gm. per second
Diameter of bar	3.80 cm.
Reading of $T_1$	79° C.
„ „ $T_2$	51° C.
Distance apart of $T_1$ and $T_2$	10 cm.
Rate of flow of heat along the bar	= $(3.417) \times (8.3)$ = 28.36 calories per sec.
Area of cross section of bar	= $\pi r^2 = \pi (1.9)^2 = 11.34$ sq. cm.
$\therefore$ Rate of flow per sq. cm.	= $\frac{28.36}{11.34} = 2.50$ cal. per second.
Temperature gradient	= $\frac{28}{10} = 2.8^\circ$ C. per cm.
$\therefore K = \frac{2.5}{2.8}$	= .89.

**Comparison of Conductivity.**—A rough comparison of the conductivities of different metals can be made by an experiment similar to that of Ingen Hausz in 1789.

A number of bars of the same length and thickness, but made of different materials, project through tubulars in the side of a rectangular metal vessel (Fig. 86). A number of marbles are stuck by means of small pieces of wax to the under side of each bar. The vessel is then filled with boiling water, and the water is maintained at the boiling-point by means of a burner; a doubled-walled screen, K, prevents the wax being melted by direct radiation from the burner. As heat is conducted along the bars, some of the marbles fall off owing to the melting of the wax; the experiment is continued until no more fall off. It will then be found that the bars have lost different numbers of marbles; in some only the first marble or two nearest the hot water have fallen, and in

of the hot end is considerably below 100° C. and that of the cold end considerably above that of the circulating water.

others considerably more. A good selection of metals to use would be copper, aluminium, zinc, iron, lead, bismuth. The effect will be much the greatest with copper and least with bismuth.<sup>1</sup> If a brass bar is included it will be found to be nothing like so good a conductor as copper, being about equal to zinc.

It is important to notice that it is the final state of the bars

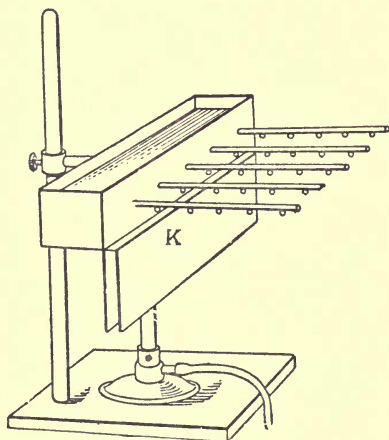


FIG. 86.

which enables us to decide which is the best conductor. When heat first begins to flow the temperature at points along a bar rises; the rate of rise depends not only on the rate at which heat is flowing, but also on the Specific Heat of the metal. Thus, the initial rate of rise of temperature along a bar of metal of low Specific Heat might be greater than in the case of a metal of high Specific Heat, even though the

latter were the better conductor. The first marbles to drop off do not necessarily come from the best conductor. But as the temperature of the bar rises it begins to lose heat to its surroundings, partly by radiation and partly by convection in the air. A steady state is finally reached when the rate of loss of heat from this cause just balances the flow of heat by conduction. Thus the amount of heat which flows across any section A of the bar is equal to the amount emitted from the surface of the bar beyond A. If much heat is flowing across A the temperature of the bar beyond will have to rise higher

<sup>1</sup> The bars should be fairly thick, e.g. about 1 cm. diameter, otherwise the worst conductors, lead and iron and possibly even zinc, will not lose any marbles at all.

than if only a little flowed, in order to get rid of this quantity. Thus, if the bar is a good conductor, the final steady temperature at any point A will be higher than at a corresponding point of a poorer conductor.<sup>1</sup> The temperature of any point of a bar is, of course, lower the further the point is from the hot end ; heat would not flow from A to a point beyond it if both parts were at the same temperature.

This method will show whether one metal is distinctly a better conductor than another, but, unless great care is taken that the surfaces of all the bars are precisely similar as regards their power of emitting heat, it does not give the ratio of the conductivities with any approach to accuracy. If the surfaces are similar, it can be shown that the conductivities are approximately proportional to the square of the distances from the hot end at which the temperature just attains the melting-point of the wax (or any other given value the same for each bar).

The absolute value of the thermal conductivity of a few substances are given below ; they represent approximate values at ordinary temperatures.<sup>2</sup>

Silver	.	.	.	.	.	.97
Copper	.	.	.	.	.	.92
Aluminium	.	.	.	.	.	.50
Steel	.	.	.	.	.	.11
Lead	.	.	.	.	.	.08
Brass	.	.	.	.	.	.26
Earth's Crust	.	.	.	about	.	.004
Glass	.	.	.	about	.	.0025, depending on the kind of glass.
Wood.	.	.	.	about	.	.0005, depending on the kind of wood.
Cork	.	.	.	.	.	.00015
Cotton Wool	.	.	.	.	.	.00004

<sup>1</sup> This assumes that the surfaces of the two bars are similar. The rate of loss of heat from a surface depends on the temperature and also on the nature of the surface: see page 214.

<sup>2</sup> More accurate values of the thermal conductivities of many substances are given in Kaye and Laby's *Tables of Physical and Chemical Constants*.



**Thermal and Electrical Conductivities.**—Silver is the best conductor of heat and is also the best conductor of electricity, with copper a close second. It is found that for metals and alloys, the ratio of the thermal to the electrical conductivity is approximately constant at any given temperature; this is known as the Weidemann Franz Law. There are, however, no substances known which act as insulators to heat in anything like the same way that such substances as glass or quartz do to electricity.

**Conduction of Heat through Liquids.**—When a liquid is heated from below, transmission of heat through the liquid takes place mainly by convection. If, however, the liquid is heated at the top, the transmission of heat downwards must take place by conduction, and it is found that the conductivity of most liquids (except mercury) is low. This may readily be illustrated by taking a boiling-tube containing water, and placing in it a piece of ice wrapped in wire gauze so that it sinks to the bottom. If the water be now heated near the top by a burner, the water at the top can be made to boil briskly for some considerable time without melting the ice. The conductivity of water at ordinary temperatures is about  $\cdot 0014$ , i.e., about half that of glass;<sup>1</sup> other liquids mostly have conductivities a good deal less than this.

**Conductivity of Gases.**—The conductivity of gases is very low; in the case of air it is somewhere about  $\cdot 00005$ ; hydrogen has a conductivity six or seven times that of air. The low conductivity of air is the reason why some materials such as blankets and woollen materials are such bad conductors of heat. They owe their properties chiefly to the numerous small air spaces in the texture of the substance. Woollen material pressed out under great pressure loses very much of its power of diminishing the transmission of heat. In the same way cotton is not a bad conductor in the ordinary way, but when made up into the form of cellular material it forms a substance which is quite suitable for use instead of woollen stuffs for clothing purposes.

<sup>1</sup> See note at the end of the chapter.

Cotton wool is another example of the effect of enclosed air.

**Transmission of Heat by Conduction. Some Practical Considerations.**—Returning to the case of the metal vessel considered on page 187. As soon as the outside is heated, heat begins to flow through the metal, and finally a steady state is reached at which the heat which flows through the metal is equal to that supplied to it by the flame. At this stage, however, the temperature of the outside of the vessel is by no means equal to that of the flame. The fact that heat is taken from a portion of the flame causes the formation of a film of relatively cool gas over the surface of the metal in contact with the flame; this film remains.

The heat from the flame has to pass through this film, and, since gas is a bad conductor, there must be a very considerable difference of temperature between the sides of the film, and this difference will be greater the greater the amount of heat flowing through per unit area.<sup>1</sup> This film of gas is a great problem to engineers, and various devices have been designed to minimize its effects.

A very simple illustration of this point is furnished by the well-known experiment of boiling water in a paper vessel. A box is made of paper, not too thick, and so long as the flame does not touch the paper anywhere above the water line or at any place where there are several folds, the water is boiled without charring the paper.

Another experiment which illustrates this point, and also the different behaviour in the case of good and bad conductors, is the following:—

A stout bar is taken, one half of which is brass and the other wood. A piece of fairly thin white paper is wrapped tightly once round the bar (the edges may overlap an inch and be secured with gum). The bar is held with its centre in the

<sup>1</sup> A similar effect is produced in the case of the experiment on page 190. When the end of the copper bar is in contact with steam, a film of moisture forms, and the temperature of the face of the copper is lower than that of the steam. In the case of a good conductor like copper the difference of temperature between the sides of the film may be greater than that between the ends of the bar.

flame of a bunsen burner. It will be found that the paper in contact with the wooden part is charred, but not that in contact with the metal. A sharp line will mark the junction of the wood and metal.

A comparatively small rise in temperature of the metal in contact with the paper results in a considerable flow of heat to the colder parts. There is therefore a considerable flow of heat across the film of gas between the paper and the rest of the flame, and so, as we have seen, there must be a large temperature difference between the flame on one side of the film and the paper on the other.

The wood in contact with the paper, being a poor conductor, will rise to a very considerable temperature before any large flow of heat to the colder parts takes place. The paper is therefore raised in temperature sufficient to char it.

**Scale in Boilers.**—Owing to the “hardness” of water a deposit known as scale tends to be deposited on the sides of boilers (similar to the “fur” in kettles). Serious consequences may occur if this is allowed. If scale is deposited on the furnace tubes, not only is the heating surface less effective, owing to the bad conductivity of scale, but owing to this bad conductivity heat does not flow through quickly until a large temperature gradient is set up, and so the part of the furnace tube in contact with the scale becomes raised to a higher temperature than the rest, in the same way as the paper in contact with the wooden part of the compound bar. The excessive expansion of this part sets up stresses, and may seriously weaken the boiler.

**Action of Wire Gauze. The Davy Safety Lamp.**—If a piece of fine-meshed wire gauze be placed over a bunsen burner (not too far above it), and the burner be lighted below the gauze, the flame will not pass through to the upper side (Fig. 87*a*); if it be lighted above the gauze, the flame does not pass down to the under side, but remains as in Fig. 87*b*.

The part of the gauze in contact with the flame loses heat by conduction to the colder parts so rapidly that its temperature is therefore not nearly so high as that of the flame, and

is, in fact, well below the ignition-point of coal gas. (In the case of a burner supplied with hydrogen, which has a lower ignition-point, the flame does pass through the gauze.) Thus any coal gas above the gauze in *a* or below it in *b* does not become ignited. It can, however, be ignited by bringing a light to it, and if this is done the flame continues to burn above and below the gauze.

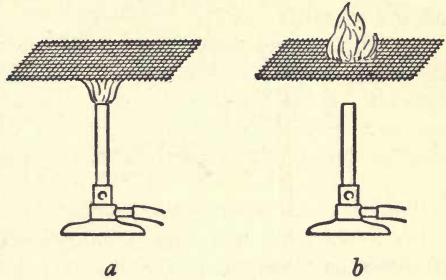


FIG. 87.

This principle was made use of by Humphry Davy in the lamp he designed for use in coal mines. The flame of the lamp is surrounded by a cylinder of wire gauze. Thus if the lamp happens to be taken into an atmosphere containing some coal gas, the gas outside the lamp will not be ignited; some of it will enter the lamp and it can be seen burning, forming a "cap" to the flame. By the look of the flame an experienced man can tell whether combustible gas is present and give a rough idea of the proportion of it.

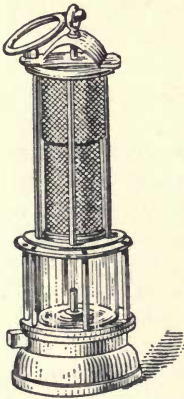


FIG. 88.

In connection with conductivity, one practical point may be noticed. It will be seen from the table on page 193 that the conductivity of the earth's crust is quite considerable. In sleeping out, therefore, the loss of heat to the ground tends to be greater than the loss in other directions, and if only limited covering is available, the greater portion of it should be under rather than over the sleeper.

**Note on the Experimental Determination of Thermal Conductivities.**—The earliest successful numerical determination

was that of Forbes, 1850. He used a bar heated at one end as in the work of Ingen Hausz, but measured the temperature at different parts of the bar by means of thermometers inserted in cavities; contact being made by filling the hole with mercury or fusible metal.<sup>1</sup>

When a steady state is reached, the heat flowing across any section of the bar is equal to that lost from the surface of the bar beyond. Since heat escapes from the sides, the amount flowing across any cross section diminishes as the distance from the hot end increases. The temperature gradient becomes therefore progressively less.

The difficulty is to determine the rate of loss of heat from the sides of the bar. This was done by a second set of experiments to determine the rate of cooling when bars of the same material and section as the original bar were heated and then left to cool. The method was very laborious, but reasonably consistent results were obtained.

Modifications of the bar method have been used in modern work on metals. The rate of flow of heat, however, is measured more directly. One way, used by Callendar and Nichols, is to measure the heat which has passed through the bar by a calorimetric method (Searle's apparatus is an example of this method).

Another way, used by Lees, is to supply the heat electrically and deduce the amount supplied.

#### Conductivity of Bad Conductors. Lees' Disc Method.<sup>2</sup>—

In outline the method is as follows. The substance was in the form of a disc 2 or 3 mm. thick and some 4 cm. in diameter.

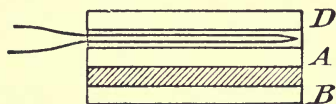


FIG. 89.

It was placed between two similar discs of copper, A and B (Fig. 89). Against the face of A is a flat coil of insulated wire which could be heated by passing a current through it. Above this is another copper disc D. A

thin layer of glycerine was used to make good thermal contact between the discs. The whole pile was varnished all over to give it a uniform surface, and was suspended in a constant-tem-

<sup>1</sup> Despretz had already used this method to verify the laws of conductivity.

<sup>2</sup> Lees, *Phil. Trans.*, 1898.



perature enclosure. A current was sent through the heating coil, and the temperature of the copper discs was determined by thermo-couples.

After a time a steady state was reached, the heat generated in the coil passing out to the surfaces of the pile, and so by radiation, conduction, and convection to the enclosure. Since copper is a very good conductor, the temperature gradient is negligible in the copper compared to that in the substance; the temperature of each disc is therefore taken as constant and given by its thermo-couple; the temperatures of the faces of the disc of substance are given by those of A and B respectively.

Since the temperatures are not high, Newton's law of cooling can be assumed; the heat lost per second per unit area of any portion of the surface pile will be some constant  $h$  multiplied by the excess of temperature of the surface over that of the enclosure.

If  $T_1$  is the temperature of D and  $A_1$  area of its exposed surface  
 $T_2$  " " " A and  $A_2$  " " "  
 $T_3$  " " " B and  $A_3$  " " "  
 and  $A_4$  the area of exposed surface of the substance the total heat lost per second is

$$hA_1(T_1 - T) + hA_2(T_2 - T) + hA_3(T_3 - T) + hA_4 \left\{ \frac{T_2 + T_3}{2} - T \right\}$$

where  $T$  is the temperature of the enclosure.

But this total is equal to the rate at which it is supplied electrically, and so is known.

This therefore gives  $h$ .

Knowing  $h$ , the amount of heat passing through the disc per second is got; it may be taken as the mean of that passing out, i.e.  $hA_3(T_3 - T)$ , and that passing in, i.e.  $hA_4 \left( \frac{T_2 + T_3}{2} - T \right)$ .

Thus the heat passing through per second is known.

The temperature gradient is  $\frac{T_2 - T_3}{\text{thickness of disc}}$

Thus we have the heat flow and the temperature gradient, and so the conductivity.

The above is a mere outline, and corrections are necessary.

**Conductivity of Liquids.**—Lees applies the method to liquids, the liquid being confined between copper discs by means of an ebonite ring. The rate of flow of heat was deter-

mined by including in the pile a sheet of substance of known conductivity.<sup>1</sup>

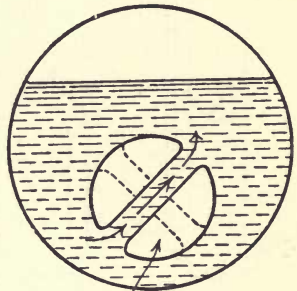
<sup>1</sup>A good account of the methods of determining conductivity is given in Preston's *Theory of Heat*, and also in Poynting and Thomson. A very complete account of the subject is given in *A Dictionary of Applied Physics*, Vol. I, published by Macmillan.

## CHAPTER XIII

### TRANSMISSION OF HEAT BY CONVECTION—SOME PRACTICAL EXAMPLES

We have already seen the large part played by convection in the transmission of heat through liquids; in the present chapter we shall consider some important examples.

**Circulation in Boilers—Use of Cross Tubes.**—In order that heat from the furnace may be communicated to the water as rapidly and evenly as possible it is necessary to have an adequate circulation of the water. The ordinary convection currents set up by the action of the furnace provide a certain amount, but the circulation is much improved by fitting a few cross tubes, as shown in Fig. 90. These tubes are inclined at an angle of about  $45^\circ$  to the horizontal, and the water in them being heated by the hot gases from the furnace becomes less dense and rises, more water flowing in from below. A very brisk circulation is set up in this way.



*Furnace tube*

FIG. 90.

**Hot-water System of Heating Buildings.**<sup>1</sup>—The boiler,

<sup>1</sup> The account in the text gives an idea of general principles, but there are several ways of applying them, and a number of important practical points arise. A standard work on the subject is *Heating by Hot Water*, Jones Walker, published by Crosby Lockwood & Sons.

An instructive article on heating and ventilating buildings is to be found in the *Journal of the Royal Sanitary Institute*, February, 1910, in which there are a number of useful diagrams.

usually of the shape shown in Fig. 91, is placed somewhere in the basement. A pipe leads out from the top of the boiler to the highest point of the system at A. From there it goes to the room or rooms to be warmed and returns to the lower part of the boiler at B.

The boiler and system of pipes are full of water, and in order that they may remain full and yet allow the water to expand a small open tank D is arranged at some level above

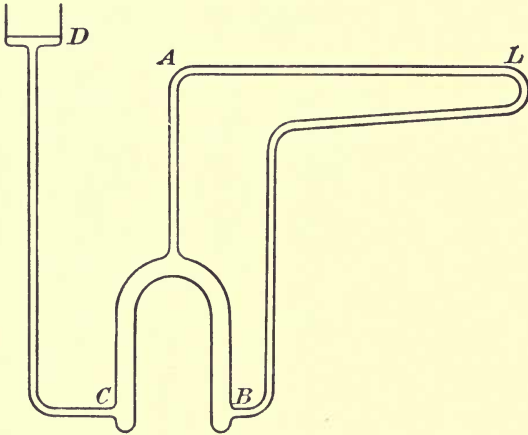


FIG. 91.

A, and communicates with the lower part of the boiler at C. The water in the upper part of the boiler and the pipe immediately above it is heated and so becomes less dense; it is therefore displaced by the colder water which flows in at B. The hot water flowing along AL gives up some of its heat to the room and so becomes colder; the circulation once set up is thus continued. Heat is supplied to the water in the boiler and some of this heat is conveyed by the circulation and given up to the rooms.

In order to increase the heating surface of the pipes a number of radiators (groups of short vertical pipes) may be included in the part AL, or the pipe may be arranged with

coils. It may be noted that the heat is delivered to the room from the surface of pipes and radiators mostly by convection currents in the air and radiation plays a comparatively small part. Where there are a considerable number of rooms to be heated the pipe branches at A to form a number of circuits, or there may be separate upright pipes from the top of the boiler. Care is necessary in designing the system, otherwise there is a much greater circulation in one route than another. Circulation is much impeded if air collects in the system, so that an air-escape valve must be fitted at the highest point (sometimes merely a vertical pipe open at the top, which must be above D) and should also be fitted at the top of each radiator.

The rate of circulation depends, among other things, on the vertical height from A to B; if the available height is small and the horizontal extent of the building considerable, convection currents are insufficient and a forced circulation is provided by a pump.

Water-cooled engines on a car provide an example of a very similar set of operations. A large amount of heat is communicated to the cylinder walls, and some of this must be got rid of if the engine is not to over-heat. The cylinders are provided with water-jackets A (Fig. 92) connected to a radiator R; the latter is essentially a tank having a top and bottom portion connected by thin metal vertical pipes between which air can pass freely as the car moves. The circulation of air is often aided by a fan driven from the engine. The connection between water-jacket and radiator is by the pipes B and C. B must start from the highest part of the jacket and slope upwards to the top of the radiator and C should slope downwards from the lowest portion of the jacket to the bottom of the radi-

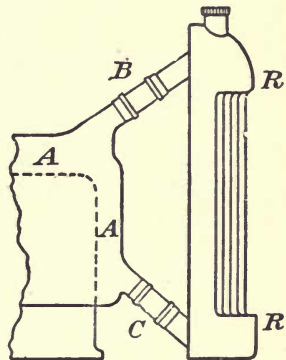


FIG. 92.



ator. The radiator and jacket are full of water ; the water, heated by the cylinder, becomes lighter and is displaced up B to the top of the radiator. Circulation is established, the heated water coming to the top of the radiator being cooled as it passes down the tubes. There is thus continual transference of heat by convection from the hot cylinder to the radiator tubes and thence to the air. This system of circulation is spoken of as the thermo-syphon principle, and it is to some extent self-regulating ; the greater the development of heat in the cylinders the more rapid is the circulation. In some cases this does not provide sufficiently rapid movement of the water and a circulating pump is provided, driven off the engine ; this applies particularly to aeroplane engines, where the problem is further complicated by the fact that the aeroplane is by no means always in a horizontal position.

**Domestic Hot Water Supply.**—Fig. 93 is a diagram showing the ordinary arrangement of the hot water supply of a house. The essential parts are the hot water cistern C, and the boiler B ; the latter is placed at the back of the kitchen fire and must be below the level of the cistern. The water in B, heated by the fire, rises up the pipe E into the upper part of the cistern, and colder water flows from the bottom of C down the pipe F into B, and becomes heated in its turn. Thus portions of heated water are constantly passing in at the top of the cistern and the colder water from the bottom passing to the boiler : more and more hot water accumulates at the top of the cistern until ultimately (if no water is drawn off) the whole of the contents become hot and then the circulation is less rapid. A pipe H near the top of the cistern leads to the hot water taps. D is a tank of cold water which communicates with the lower part of the cistern and provides the necessary pressure to drive out the hot water when the taps are opened ; the colder water flowing in. As the water flows out of D the float K descends and opens the valve L which admits more water from the supply until the level is restored. The open pipe G is a

safety outlet in case the water in the cistern becomes so hot as to boil.

In the above examples we have been concerned with convection currents as a means of transferring heat from one place to another: there are, however, many cases where the interest from a practical point of view is centred in the actual movement of the liquid or gas rather than in the transference of heat. Examples of such cases are the action

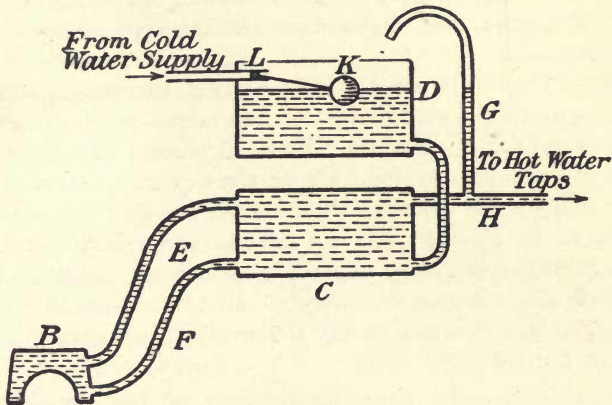


FIG. 93.

of chimneys, ventilation of buildings and atmospheric movements such as the Trade Winds.

**Action of Chimneys.**—The gases in a chimney above a fire are hotter than the air outside it, and consequently have expanded and become less dense.<sup>1</sup> The pressure at the base of the chimney due to these lighter gases is less than that of

<sup>1</sup> The gases in the chimney will include the products of combustion some of which, e.g. CO<sub>2</sub>, are heavier than air at the same temperature. On the other hand some, e.g. water vapour, are lighter, and the largest part (residual nitrogen) about the same density. The great bulk of the products at the high temperature will be considerably lighter than the outside air, and even CO<sub>2</sub> does not require to be at as high a temperature as 200° C. to be lighter than air at 15° C. and the same pressure. Under natural draught 1 lb. of coal requires at least 24 lb. of air, so that 24 lb. of air only make 25 lb. of products of combustion.

the air at the same level ; the latter therefore flows into the chimney above the fire and through the grate displacing the lighter gas. This air becomes warmed in turn, and so a circulation is set up. This circulation is of the utmost importance in getting the fire to burn. For example, it sometimes happens that when a domestic fire is first lighted difficulty is experienced in getting it to start : the fire will not " draw " and shows a tendency to smoke into the room. Warming the air in the chimney (e.g. by burning paper) will often start the circulation in this case, and the fire will then burn satisfactorily.

When the fire in a room is well alight, the quantity of air passing up the chimney is very considerable—much more than is required for combustion. Fresh air comes into the room by any available openings, e.g. at the top and bottom of the door and by the windows (if the latter are shut they are not likely to be air-tight and air gets in through the chinks). In this way a fire is an important ventilating agent, and its merit is that air does definitely go out of the room and fresh air comes in ; it is not merely a case of setting up circulation within the room.

**Ventilation.**—In the consideration of the problem of ventilation the properties of convection currents must be considered not only with regard to the main movement of the air, but also in connection with local effects. Any object which warms the air in its neighbourhood results in an upward air movement, and equally any cold object results in a downward current. For example, large windows, even if closed, mean a surface which in cold weather is colder than the rest of the walls, so that the air inside tends to be cooled and quite a considerable down-draught of cold air may be set up. This effect is so noticeable in some cases, e.g. churches, that pipes have to be arranged near the wall to warm this air and prevent the down-draught. Again, each person to some extent produces his own ventilation current ; he warms the air in his neighbourhood, and the air he breathes out is warmer (and contains more water vapour but also more

carbon dioxide) and so tends to rise out of the way. If it were not for this effect any one sleeping in bed would tend to surround himself with a layer of unbreathable air. Thus vitiated air tends to rise to the upper part of the room, and the problem is to arrange for its removal and replacement.

The effect of an open fire in renewing the air of a room has already been mentioned; if, however, the entering air merely comes in at doors and windows it will tend to sink and travel as a cold current near the floor direct to the fire-place, leaving the upper air undisturbed. A common arrange-

ment intended to assist the displacement of the upper air is to bring in the entering air by a Tobin tube (Fig. 94) delivering above the heads of the occupants; if, however, the air is cold it will still sink when it gets in. A more successful arrangement is to allow the entering air to be warmed by passing over a heated surface, in which case it is more effective in sweeping out the vitiated air, since it no longer sinks to the floor level.

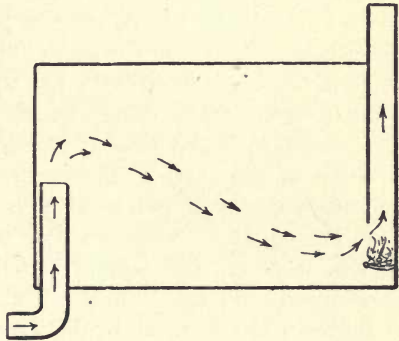


FIG. 94.

A common method of getting air to enter in the case of large halls heated by radiators is to have a row of radiators along a wall and air inlets behind them; the radiator causes an upward convection current and fresh air enters through the inlets and is warmed in turn.

In some systems of ventilation the used air is extracted (by means of fans or by a heating arrangement in an external flue) causing a reduction of pressure so that fresh air enters automatically where it can; another system (the plenum system) delivers fresh air through inlets and causes a slight excess of pressure so that used air is driven out; neither of

these systems can be regarded as very satisfactory, and it is better to have two separate arrangements, one driving in fresh air and the other extracting used air.

It may be mentioned that, considered solely from the point of view of setting air in motion, direct heating is much less efficient than using the heat in an engine and moving the air by a fan.<sup>1</sup>

**Trade Winds.**—Convection currents in the atmosphere play a most important part; as an example, the Trade Winds may be considered. Owing to the higher temperature in the equatorial regions of the earth, convection currents are set up, colder air flowing in from the north and south temperate regions near the earth's surface and a corresponding current flowing outwards in the upper air. The lower currents form the Trade Winds, which blow with great regularity. The direction is not exactly north and south, owing to the rotation of the earth; the earth rotates from west to east and the velocity of points at high latitude is less than those near the equator. Consequently the wind from the regions of less velocity lags behind the regions of higher velocity and appears to come from the N.E. and S.E. respectively.

Between the N.E. and S.E. Trade Winds is the region of the equatorial calm where the ascending current is taking place.

<sup>1</sup> An admirable account of the principles of ventilation is given in *Air Currents and the Laws of Ventilation*, W. N. Shaw, Cambridge University Press, in the course of which it is shown that some forms of ventilation systems give most unexpected and rather humorous results (from the point of view of outside observers).



## CHAPTER XIV

### RADIATION

Of the two processes by which heat may be transmitted from one place to another, the two already considered (conduction and convection) have a certain resemblance; the whole or part of the medium between the places is heated, and some time elapses before the operation is completely established. But the process known as radiation is altogether different; it goes on most readily when there is no material medium between the places (i.e. across a vacuum) and with very great velocity.

That conduction and convection are not the only means by which a hot body can lose heat is illustrated by the following simple and rather rough experiment. The hot body is a glass bulb blown on the end of a piece of thick-walled narrow-bore tubing and filled with mercury so that it is like a large thermometer; it can be made to indicate its own temperature by the position of the mercury in the tube.

Two metal vessels, of the same size, shape, and material (e.g. copper calorimeters), are provided; the interior of one vessel is highly polished, and that of the other coated with a layer of lampblack by holding it over the flame of burning camphor. The tube of the "hot body" passes through a rubber cork fixed in a hole in the centre of a piece of stout

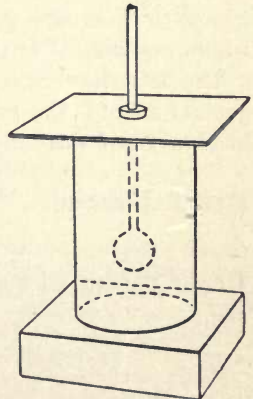


FIG. 95.

P

cardboard (Fig. 95); the position of the cork is adjusted so that when the cardboard is placed on the mouth of one of the metal vessels the bulb will reach nearly to the bottom. Two or three fine scratches are made on the tube

about 1 cm. apart and rather nearer the upper end; the bulb should also be coated with lamp-black. The hot body is heated by placing it in a metal cone on a sand bath (Fig. 96); it is allowed to remain there until the mercury is some distance above the upper mark. It is then transferred to the polished metal vessel, and the time at which the mercury passes each mark noted by a stop-watch or an ordinary watch with seconds hands. The hot body is then transferred to the heater again and heated until the mercury is above the upper mark; it is then placed in the blackened vessel and the time at

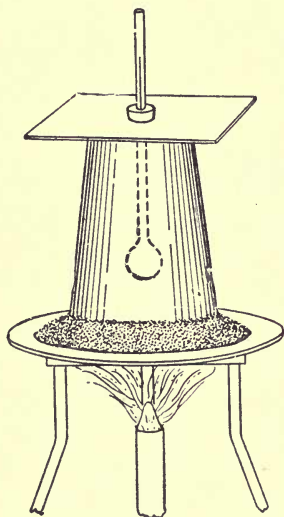


FIG. 96.

which the mercury passes each mark is again noted. The whole experiment is then repeated.

The following readings from an experiment indicate the general effect: the first two marks were about 1 cm. apart, but the third was only about 0.5 cm. below the second.

### First Experiment.

	Polished vessel.	Black vessel.
	m. s.	m. s.
Time of passing 1st mark .	0 18	0 9
„ „ 2nd „ .	1 25	1 1
„ „ 3rd „ .	2 10	1 38
	Total 1-3=	Total 1-3=
	1 m. 52 secs.	1 m. 29 secs.

## Second Experiment.

	Polished.	Black.
	m. s.	m. s.
Time of passing 1st mark .	0 40	0 43
„ „ 2nd „ .	1 49	1 38
	1 m. 9 s.	55 secs.
„ „ 3rd „ .	2 39	2 15
	50 secs.	37 secs.
	Total 1-3=	Total 1-3=
	1 m. 59 secs.	1 m. 32 secs.

It will be noted that in every case the time taken for the mercury to fall from any one mark to another was distinctly greater when the bulb was in the polished enclosure than when it was in the blackened one. Now when the mercury is at any particular mark the temperature must be some particular value. Hence passing from one mark to another represents a definite fall in temperature, and since we are always dealing with the same mercury and bulb this represents the evolution of a definite quantity of heat. Thus the rate of loss of heat is smaller when the bulb is surrounded by the polished vessel.

The bulb loses heat by conduction and convection through the air, and conduction through the glass stem, cork and cardboard.

But the conditions are similar in the two cases; there is no reason to suppose that the lampblack surface would increase the convection, and certainly none for supposing it to increase conduction.

The bulb must therefore in addition lose heat by other process involving the emission of something which can be reflected. This part of the loss is the radiation,<sup>1</sup> and the

<sup>1</sup> In order that the radiation loss may be a considerable fraction of the total heat loss, the temperature of the hot body should be fairly high. In the above apparatus the quantity of mercury was adjusted so that the upper mark corresponded to a temperature of about 150° or 200° C. It is desirable to have a considerable mass of mercury; the bulb in the hot body used was 3 cm. in diameter, and the vessels were thin copper calorimeters 10 cm. high and 6.4 cm. diameter (4 in. × 2½ in.). The blackened vessel at the end of an experiment was always perceptibly hotter than the other.

something emitted is often referred to as "radiant heat"; this term, however, is not a very happy one, and although we shall make use of it for the present, we shall see later that there is an expression for it which conveys a better idea of its true nature (page 226).

This radiant heat has many properties in common with light; it travels through any homogeneous medium in straight lines and obeys the same laws of reflection as light. In order to illustrate these properties we shall require something with which to detect the radiant heat; for this purpose

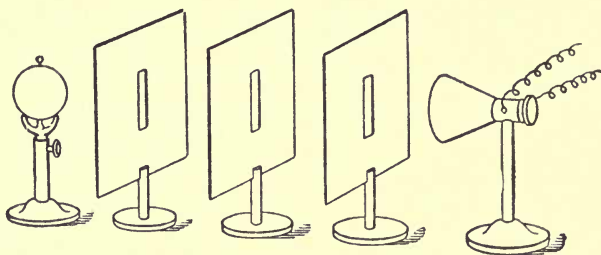


FIG. 97.

a thermopile (page 5) is convenient,<sup>1</sup> and in order to get considerable deflections on the galvanometer scale it should be fitted with a cone polished on the inside. Three pieces of stout card are taken, and in each of them is cut a slit about .5 cm. wide and of length equal to the diameter of the large end of the thermopile cone. The cards are mounted vertically on stands, and placed in such a position that the slits are accurately in line; this is determined by sighting from one end.

The cone of the thermopile is placed immediately behind the last slit, and a large copper ball, previously heated over a gas ring, is placed on a stand in front of the first slit (Fig. 97). A considerable deflection of the spot of light on the galvano-

<sup>1</sup> An air thermometer can be used in some cases, and was used in early experiments on radiation. It is not, however, sufficiently sensitive for many of the experiments here described.

meter scale will be noticed; but if the centre card be displaced sideways so that the slits are no longer in line, the spot of light moves back.

Fig. 98 shows the arrangement for illustrating the laws of reflection. The third screen is moved from its place in line with the others and placed in some such position as B. A

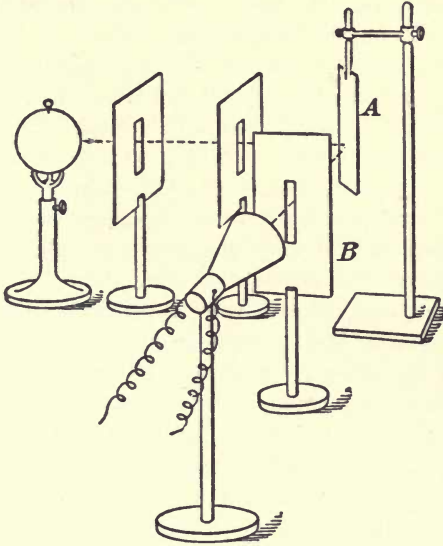


FIG. 98.

strip of polished metal *A* is mounted on a stand so that it can be rotated about a vertical axis. It is placed in line with the first two slits, and then rotated until an observer looking through the slit in *B* sees the reflection of the first two apparently in line. The thermopile is placed behind the slit in *B*, and the hot ball behind the first. A deflection of the spot of light on the galvanometer scale is noticed, and a rotation of *A* either way causes the spot to move back.<sup>1</sup>

<sup>1</sup> The screens should not be too far apart unless the galvanometer is very sensitive. The writer finds that with a 20 element thermopile and a Paul reflecting unipivot galvanometer good deflections are got with the screens about 6 cm. apart, using slits .5 cm. wide.



**Emissive Power of Various Surfaces.**—The intensity of the radiation from the hot object depends not only on the temperature, but also to a very large extent on the nature of the radiating surface. This was established by Sir John Leslie and may readily be shown by using a Leslie cube—a cubical tin vessel which can be filled with hot water and of which the sides can be coated with any desired substance. One side should be coated with lampblack so as to give a dull black surface, another should be highly polished, while the other two sides may be respectively roughened and painted white. If such a cube be filled with boiling water and placed near a thermopile, it can be rotated so as to bring each face in succession opposite the thermopile and the deflection of the spot of light on the galvanometer scale noticed; care must be taken not to vary the distance between the cube and the thermopile as the former is turned. It will be found that much the smallest deflection is given when the polished face is radiating to the thermopile while the largest is given by the dull black face; the other two faces will give intermediate deflections, the white painted surface giving the larger. All experiments show that a highly polished metallic surface is an exceedingly poor radiator, while the best of all radiators is a perfectly dull black surface.

**Absorbing Power of Surfaces.**—When radiation falls upon any object some or all of it may be absorbed, and the absorbed energy then appears as heat in the ordinary form; it is not until it has been absorbed that the ordinary effects of heat are manifested. The extent to which absorption takes place depends very much on the nature of the surface. A highly polished metallic surface will reflect most of the radiation which falls upon it and absorbs very little; the metal will therefore be very slightly heated. On the other hand, a dull black surface absorbs practically all the radiation which falls upon it, and the heating effect is correspondingly greater.<sup>1</sup> This may be illustrated by the following experiment (Fig. 99):—

<sup>1</sup> Cp. footnote on page 211.

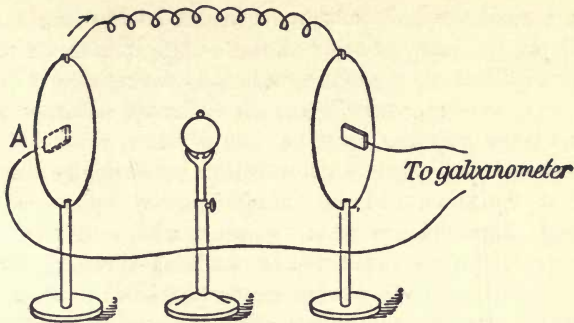


FIG. 99.

Two large tinned iron discs are mounted on stands to face each other. The face of one disc is polished and that of the other is coated with lampblack. On the back of each disc, in the centre, is soldered a bar of bismuth. Each piece of bismuth is connected by a wire to one terminal of a galvanometer and the circuit is completed by a wire connecting the two discs. There are thus in the circuit two bismuth-iron junctions; if either junction is heated, a current tends to flow round the circuit. But whereas the junction at A when heated tends to make the current flow in the direction of the arrow, the other junction when heated tends to make it flow in the other direction; <sup>1</sup> thus, if both junctions are equally heated no current will flow. A hot copper ball is placed on a stand midway between the discs, and it will be noticed that the spot of light at once begins to move on the galvanometer scale, showing that one junction is hotter than the other. If, however, the hot ball is moved nearer to the polished disc, the spot of light moves back and a position can be found, much nearer the polished plate than the black plate where there is no galvanometer deflection.

Thus it appears that when the two discs are receiving similar amounts of radiation, the black surface absorbs a greater proportion than the bright and so becomes hotter;

<sup>1</sup> With a bismuth-iron junction the direction of the current is from bismuth to iron across the hot junction.

it is not until the ball is brought nearer to the bright plate, so that the intensity of the radiation upon it is much greater than that falling on the black, that the heating effects become equal. By coating the discs with different substances, the effects of the surfaces may be compared.

It is found that there is a connection between the absorbing power of a surface and its emissive power; surfaces which are good absorbers are good radiators also, and vice versa; moreover, accurate experiments, such as those of Melloni, show that the emissive powers are proportional to the absorbing powers, i.e. if one surface absorbs, say, 50 per cent. of the incident radiation and another 25 per cent., then the

surface will radiate twice as much as the other under the same conditions.<sup>1</sup>

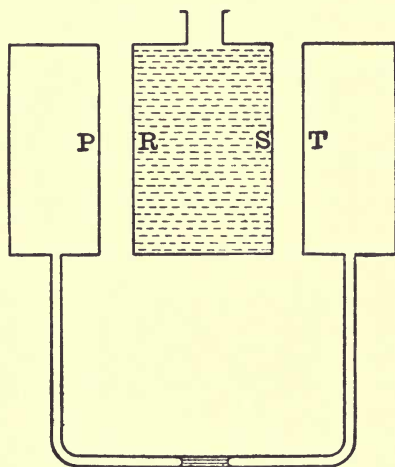


FIG. 100.

liquid to the right, while if T is heated the liquid moves

A well-known piece of apparatus to illustrate this point is represented in Fig. 100. P and T are two similar airtight tins, connected together by a glass U-tube in which is contained some coloured liquid. The whole forms a differential thermometer; if P is heated the air in it expands, driving the

<sup>1</sup> This statement requires a certain amount of qualification. If the surfaces absorbed respectively 50 per cent. and 25 per cent. of the radiation from a Leslie cube at 100° C. they would not necessarily absorb the same fractions of the radiation from a copper ball at 300° C. nor would one fraction be twice the other. But the radiating powers of the surfaces would also be different at 300° C. from what they would be at 100° C.; the radiating and absorbing powers would correspond to one another at 300° C. and also at 100° C.

in the other direction. If both are heated to the same temperature the liquid remains in its original position. The surfaces of the ends of P and T which face inwards are treated differently, e.g. one may be highly polished and the other lampblacked, or one may be painted. RS is a cylindrical tin, which can be filled with hot water, mounted midway between P and T and arranged so that it can be rotated about a vertical axis. The surfaces of the ends of RS are made similar to those of P and T, but if, for example, P is polished and T is black, then R is black and S is polished. On pouring hot water into RS, no movement of the liquid in the air thermometer takes place; the radiation from R is greater than that from S, but the smaller absorbing power of P and the greater absorbing power of T just compensate the effect. If, however, RS is rotated so that the two blackened surfaces are opposite, a considerable movement of the liquid takes place.

At this stage it is convenient to consider for a moment the action of the thermopile. When the radiation falls upon one end most of it is absorbed and the absorbed radiation is converted into heat. The temperature of the receiving end therefore rises, and continues to do so until the rate of loss of heat to the surroundings is equal to the rate of supply of heat by absorption of the radiation, when the temperature remains steady and the deflection of the galvanometer is constant. The final value of the deflection is thus a measure of the rate at which the thermopile is absorbing radiation, but the time taken to reach this final value depends on the mass of metal in the instrument and has nothing to do with the time taken by the radiation in passing to it from the hot body. It will have been noticed that the spot of light on the galvanometer scale *begins* to move immediately a hot object is brought near, and in the case of the more accurate instruments, the radio-micrometer and the bolometer, in each of which the absorbing parts are of extremely small mass, the indications are practically instantaneous. As we shall see later, there is every reason to believe that radiant

heat travels with a velocity similar to that of light (186,000 miles per sec. in vacuo, and somewhat less in air or other substances).

**Diathermanency.**—Hitherto we have dealt only with objects which absorb any portion of the incident radiation which is not reflected from the surface. Some substances, however, will allow radiation to pass through them. A substance through which radiant heat can pass is spoken of as diathermanous, while one through which radiant heat cannot pass is said to be adiathermanous. These terms correspond to the expressions transparent and opaque in the case of light; a substance through which light can pass is transparent, while one through which radiant heat can pass is diathermanous. It does not by any means follow that a transparent substance is diathermanous (e.g. glass is very adiathermanous), nor that an opaque substance is adiathermanous.

Some of the more important points may be illustrated by the following method: In front of a thermopile, and a few centimetres away from it, is placed a metallic screen with a hole in its centre; the hole should be considerably smaller than the cone of the thermopile so that all radiation coming through is collected by the cone.

A hot object, such as the hot copper ball, is placed at such a distance from the opposite face of the screen as to give a convenient deflection on the galvanometer scale. Plates of different materials, of as nearly as possible the same thickness, are placed in succession between the screen and the thermopile so as to cover the opening but not touching the screen. If a glass plate is interposed between screen and thermopile the spot of light on the galvanometer scale will move back nearly to zero; the effect is even more marked if the source of radiation is the blackened face of a Leslie cube filled with boiling water. Glass is thus very adiathermanous. A plate of alum will also be found to be very adiathermanous. On the other hand, with a plate of



rock salt,<sup>1</sup> the deflection is not much less than with the open hole, showing that rock salt is extremely diathermanous.

Another very diathermanous substance is a solution of iodine in carbon di-sulphide, a solution which is opaque to light. If a very thin-walled flask be placed empty between the screen and the thermopile and the deflection of the galvanometer noted (if the glass is very thin a reasonable deflection will be obtained), and the flask be then filled with the solution of iodine the deflection will be very little diminished.

Water, on the other hand, is very adiathermanous, but the presence of substances in solution appears to increase the diathermanency; even a solution of alum is more diathermanous than pure water although the idea is still sometimes met with that such a solution is one of the best adiathermanous media.

We have just seen that glass is very adiathermanous; on the other hand, the action of a convex lens as a "burning glass" is a well-known phenomenon. If a sharp image of the sun is focussed, by means of a convex lens, on to a piece of paper, the latter will be charred and may even burst into flame. There is no question about the development of heat; if the hand be substituted for the piece of paper, the fact is at once apparent. We can make the behaviour of the glass more obvious by a further experiment with the apparatus of the preceding paragraph. Place the hot copper ball at such a distance from the screen as to give a suitable deflection on the galvanometer scale, and observe that if a glass lens be placed between the aperture of the screen and the thermopile, the spot of light goes back nearly to zero. Remove the lens,

<sup>1</sup> The surface of rock salt tends to become pitted when exposed to moist air owing to the hygroscopic nature of the salt; for this reason such plates are often supplied sealed between two glass plates. It will be obvious that as glass is very adiathermanous, these plates must be removed in the above experiment if the effect of the rock salt is to be seen.

and substitute for the copper ball an arc lamp,<sup>1</sup> placed at such a distance from the screen as to give about the same deflection on the galvanometer scale as was obtained from the ball.

If now a slab of glass several centimetres thick be placed between the screen and the thermopile, it will be noticed that the deflection of the galvanometer is very little less than without the glass. But if in addition a flask of iodine in carbon di-sulphide be placed between the glass and the thermopile, the spot of light will go back nearly to zero. Thus in the case of the arc lamp we are getting results which are almost exactly the converse of those with the copper ball.

Now the experiments with the copper ball showed that radiant heat passed through the iodine solution, but not with any readiness through glass ; on the other hand, we can see that light passes through glass but not through the iodine solution. It looks then as if light affects a thermopile in the same manner as radiant heat, and in fact all experiments show that this is so.<sup>2</sup> For this reason the term "radiation" is used in a general sense to include both light and what we have called radiant heat ; when radiation of any sort falls upon a surface some or all of it may be absorbed and that part which is absorbed is in general<sup>3</sup> converted to heat.

At this stage it will be convenient to consider some properties of radiation ; in the course of this consideration two important points will emerge, i.e. that just as light may be of different colours, such as red or blue, so radiant heat may have different characteristics ; and further, radiant heat and light are not two sharply distinguished kinds of radiation, but the one merges into the other so that the boundary between them is not easy to define, and, indeed, depends to some extent on the observer. Anything like a full considera-

<sup>1</sup> The arc lamp will probably belong to an optical lantern, and it is convenient to keep it inside the lantern body (to avoid an intolerable glare in the room) but the condenser and all lenses must be removed.

<sup>2</sup> Cp. footnote, page 225.

<sup>3</sup> An exception occurs in the case of fluorescence, where some part of the absorbed radiation is converted to radiation of a different type.

tion involves the whole subject of spectroscopy and the following treatment is only to be regarded as the barest outline. We shall first deal with some properties of light and then show how these properties extend to radiation in general.

If a narrow beam of light falls upon a prism of glass in a direction such as  $AB$  (Fig. 101), it will suffer refraction at the

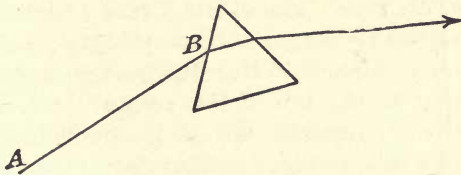


FIG. 101.

two faces ; that is to say, it will be bent (towards the thick part of the prism) and come out in a direction making a considerable angle with  $AB$ . The angle will depend on the particular prism used, but it will also depend on the colour of the light. A convenient experimental arrangement for illustrating this point is shown in Fig. 102. A metal screen, with a narrow vertical slit  $A$ , is arranged as shown, and

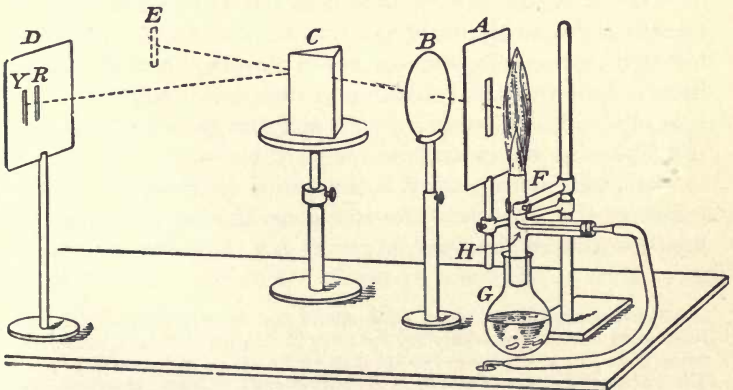


FIG. 102.

behind it sources of light of different colours will be placed in succession.

B is a convex lens adjusted so that if no prism were there it would form a real image of the slit at about the position E. When the prism C is in position, the light will be bent and the image of the slit can be received on a screen at D. The arrangement for getting lights of different pure colours is shown in the diagram. F is a silica T tube ; in the side tube is fixed a narrower tube connected to the gas supply and furnished with a small hole at H. The gas issues from this hole and is lighted at the top of the vertical branch of the T, forming a sort of bunsen burner. G is a small flask containing a solution of a salt, to which is added some hydrochloric acid and a few pieces of magnesium ribbon. The magnesium dissolves with a brisk evolution of hydrogen, causing a spray of the salt solution to pass up to the flame and colour it. The colour depends on the salt in solution.<sup>1</sup>

If a flask containing a solution of lithium chloride be placed under the T tube, a pure red colour is obtained and the red image of the slit will be seen on the screen in some such position as shown at R. If this position be marked, and (without moving any other part of the apparatus) a flask with a solution of common salt be substituted for the lithium chloride, a yellow light is obtained, but the yellow image of the slit is not in the same position on the screen ; it will be found in some such position as Y, showing that the yellow light is bent through a larger angle than the red.

If now a flask containing both salt and lithium chloride be substituted a yellow and red image of the slit will be formed in the positions Y and R ; the prism sorts out the mixed colour of the flame into the two constituents. Blue light is bent even more than yellow ; it is not, however, so easy to

<sup>1</sup> This arrangement, very convenient for spectroscopic work, has been used most successfully by Prof. T. R. Merton. It is described in some detail in a lecture given by him of which an abstract appears in *The School Science Review*, February, 1921. John Murray. The dimensions of the apparatus are important.

get a salt which gives a blue light intense enough to show up well on the screen. But if a Geissler discharge tube containing hydrogen be substituted for the flame, the mixed colour will be sorted out by the prism into a red image (not quite in the same position as the lithium red, which is of a slightly different shade), a greenish blue image beyond the position of the sodium yellow, and a blue image beyond that. There is a violet image beyond that, but it is not very easy to see and may be missed. Thus light of each colour is bent through a definite angle, so that each colour gives rise to an image in a definite position.<sup>1</sup>

If now we substitute for the coloured flame a source of white light such as an arc lamp, we do not get a single white image of the slit on D, but a band of colour, one end of which is red shading off gradually to orange, the orange to yellow, yellow to green, green to blue and blue to violet, the latter forming the other end of the band. Such a band of colour is known as a continuous spectrum and represents an indefinite number of overlapping images of the slit. It appears then that white light is complex and the prism is able to sort out from it all these different colours.<sup>2</sup> Each kind of light bends through its own particular angle and gives its own definite image on D, and the position of the image identifies the particular kind of light.

It has already been mentioned that light affects a thermopile or similar instrument, and we can make use of this effect to learn a good deal more about the spectrum. An ordinary thermopile is not suitable for this purpose, since it would cover too large a part of the spectrum at once. A more suitable instrument is a Rubens linear thermopile, with the junctions arranged in a single vertical row; a bolometer or a radio micrometer would generally be used in accurate work.

By making a slit in the screen D, not quite so wide as the

<sup>1</sup> Provided that we keep to the same prism throughout and do not alter the direction in which the incident light meets the prism face.

<sup>2</sup> Strictly speaking the matter is not so simple, and modern work, begun by Gouy as far back as 1886, shows that the action is not a mere sorting out of colours already there.



height of the spectrum but extending well beyond it at each end, and placing the linear thermopile behind it, we can examine the heating effect at each part. It will be found that when the thermopile is in the violet part the heating effect is small, but as it is moved towards the red end the effect is increased. As the instrument is moved out beyond the red end there is no sudden change; a heating effect is found in a region extending well beyond the visible spectrum. As the movement is continued the heating effect gradually diminishes and finally becomes incapable of detection. The radiation from the arc lamp is thus sorted out by the prism into a long spectrum, part of which is visible and part invisible.

The invisible spectrum must consist of parts of different qualities corresponding to the different coloured lights, for the parts of the invisible radiation are bent through different angles.

Now the study of the properties of light (chiefly the phenomena of interference and diffraction) led to the conclusion that light is some form of wave motion. As, however, it travels across a vacuum, it cannot be a wave motion in a material medium such as is met with in the case of sound. But a wave motion implies some medium for its transmission, and so there was developed the idea of a medium filling all space. This medium is spoken of as the æther, and light is regarded as some form of wave motion in the æther.<sup>1</sup> The different coloured lights are regarded as being of different wave lengths (the distance from one wave to the corresponding point on the next). These wave lengths have been measured by means of diffraction gratings and later by more accurate methods, and it is found that the wave length of red light at one end of the spectrum is nearly twice as great as that of violet at the other, the values being about  $\cdot 00077$  mm.

<sup>1</sup> The precise meaning to be attached to the term æther is a question far beyond the scope of this book. The wave motion is almost certainly some form of electro-magnetic disturbance, but the precise method of its propagation is a matter difficult to decide.

and 0.004 mm. respectively. Intermediate colours have wave lengths somewhere between these amounts. Thus white light may be regarded as containing radiation of all wave lengths between these limits and the prism sorts them out and sends them in different directions, like a policeman directing traffic.<sup>1</sup> The thermopile indicates that the spectrum does not end at the red, but extends without interruption for some distance beyond; in this case there is no distinction between visible and invisible radiation.<sup>2</sup>

This leads to the conclusion that the invisible radiation is similar to light, i.e. some form of wave motion in the æther, but of wave length ranging from that of the extreme red light to greater values. Measurements made by Langley (*Phil. Mag.*, 1884 and 1886) with a diffraction grating used in the same way as in the case of light, determined some of these longer wave lengths and many others have been made subsequently. The radiation from a source such as an arc lamp must be regarded as made up of constituents having every wave length between certain limits. All of this radia-

<sup>1</sup> The really essential characteristic of any light is not so much the wavelength as the frequency, i.e. the number of waves passing a given point per second. So long as the light moves in one medium it does not matter whether we deal with frequency or wave length, but if the light passes from one medium to another the wave length changes while the frequency does not.

Since the frequency is the number of waves passing a given point per second it follows that frequency  $\times$  wave length = distance the light travels in unit time, i.e. the velocity.

<sup>2</sup> At one time the view prevailed that light did not itself produce heating effect, but that this was due to a separate kind of radiation. When it was found that after sorting out the radiation with a prism a heating effect was still observable in the visible part, it was thought that possibly there was some portion of invisible radiation which could not be separated from the light by the prism. To settle the point M. Jamin (*Comptes Rendus*, 1850) allowed a beam of the light from one portion of the spectrum to pass through various absorbing media, and made measurements: (a) by a photometer of the diminution of the light, (b) by thermopile of the diminution of the heating effect. He found that in all cases the percentage of diminution of the heating effect was equal to that of the light and concluded therefore that heating and light were merely properties of the same radiation. An account of this work is given in the admirably clear "Études des Radiation" in M. Jamin's *Cours de Physique*, 1891, tom. 111.

tion affects a thermopile, but some of its properties depend on the particular wave length, and only those parts of it are visible of which the wave length is less than about  $\cdot 0008$  mm. ; the precise value of this limit is found to vary slightly for different people. All this invisible radiation of wave length greater than about  $\cdot 0008$  mm. is spoken of as infra red radiation, a much more satisfactory expression than radiant heat.

#### **Transmission of Radiation through Different Media.**

—As soon as it is realized that radiation may have different characteristics according to its wave length, many of the apparent anomalies in connection with diathermanency and adiathermanency are accounted for. Many substances will allow radiation of certain wave lengths to pass through them, but absorb strongly radiation of all other wave lengths. Glass readily transmits radiation of all wave lengths between about  $\cdot 0004$  mm. and  $\cdot 002$  mm., that is to say, all the visible radiation and a considerable range of the infra red, but absorbs strongly anything of longer wave length. Alum transmits the visible radiation, but very little else.

Iodine in carbon di-sulphide transmits the long wave radiation but absorbs the visible. Rock salt appears to transmit all radiation readily,<sup>1</sup> and so also does sylvine (potassium chloride).

**The Connection between the Temperature of a Body and the Characteristics of the Radiation it Emits.**—Not only does the total amount of radiation from a hot object depend on the temperature, but the character of the radiation varies also. For example, suppose we have a copper ball at a temperature of about  $100^{\circ}$  C. It is obviously not luminous, but the radiation can be sorted out into a spectrum (but it will be necessary to use a lens and prism of rock salt, since glass absorbs the long wave radiation) which can be explored with a linear thermopile or a bolometer.

<sup>1</sup> It absorbs strongly the particular type of radiation given off by another heated piece of rock salt; this is a particular instance of a well-known phenomenon met with in spectroscopy.

The spectrum will not be very long, and its position will indicate that it is composed of relatively long wave-length radiation. If the temperature of the ball be raised, exploration with the thermopile will show that the spectrum has lengthened out in the direction of the visible, showing that the radiation now contains some shorter wave-length constituents.

If the temperature is raised still further the spectrum lengthens out, and at something like  $700^{\circ}\text{C}$ . it just reaches the position of the extreme red and the ball begins to appear a dull red. At higher temperatures other components of the visible spectrum appear, and at something like  $1,300^{\circ}\text{C}$ . all the colours are present and the ball is "white hot."

With a source of radiation at still higher temperature, such as an arc lamp, it is possible to detect an extension of the spectrum beyond the violet. As a rule only the most sensitive of radiometers will detect the heating effect of this very short wave-length radiation, and of course it is not visible. It can, however, be detected by its action on a photographic plate or by allowing it to fall on a fluorescent screen such as is used for X-ray purposes. This radiation is spoken of as ultra violet radiation.

Glass is very opaque to ultra violet radiation, but rock salt and sylvin transmit it readily, as does quartz.

There is one point in connection with the radiation spectrum of a hot body which is of great importance in practical problems of illumination.

If the radiation from such a body be spread out into a spectrum by means of a prism (of rock salt or fluor spar) and the spectrum be explored with a bolometer or linear thermopile, the reading of this instrument will be a maximum in one position and will gradually diminish to zero as it is moved away in either direction. If the readings of the thermopile are plotted for the different positions the curve would be something like Fig. 103, ABC. If now the temperature of the body be raised and the spectrum again explored, the result will be as indicated by DEF. In this curve it will be

seen that the spectrum extends further into the shorter wave-length region, and that the position of maximum energy corresponds to a shorter wave length than in the case of ABC. Notice, however, that the whole of DEF is above ABC, i.e. the body does not cease to give out the long wave-length radiation; in fact it gives out rather more, but there is a more than proportionate increase in the amount of short wave radiation. The higher the temperature of the body the

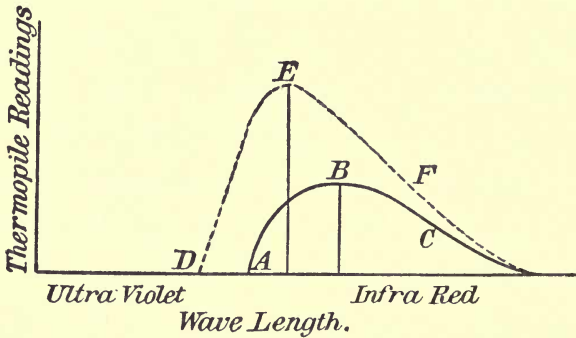


FIG. 103.

further up the spectrum does the position of maximum energy appear. In the case of the sun, whose effective temperature (see page 253) is probably somewhat under  $6,000^{\circ}\text{C.}$ , the position of maximum energy is in the yellow of the visible spectrum; a body at  $1,500^{\circ}\text{C.}$  would give the position of maximum energy not in the visible spectrum at all but well in the infra red.

Now the total energy radiated will be proportional to the area under the whole curve, while the amount of light (the part of the radiation which is visible) will be proportional to the area under the curve between the values of the wave-length which correspond to the upper and lower limits of the visible spectrum. If the position of maximum energy is well in the infra red it is clear that very little of the total radiation is light, while if the position of maximum energy is somewhere near the middle of the visible spectrum, a large pro-



portion of the whole radiation will be light ; this is in fact the condition in the case of the sun's radiation. Thus the higher the temperature of a body the greater will be the proportion of its total radiation which is in the form of light (unless indeed it were hotter than the sun, a condition not likely to be realized).

The arrangement in an ordinary incandescent electric lamp is to send a current through a thin wire or filament enclosed in a glass bulb. The electrical energy is converted to heat and the wire becomes white hot ; its temperature depends on the length, material and thickness of the wire. The amount of electrical energy used will be proportional to the total emission of heat from the wire, and as we have just seen the proportion of this energy which appears as light increases as the temperature is raised. The lamp will therefore be more efficient the higher the temperature at which it is arranged that the filament shall be. The difficulty is to find a material which is able to stand a very high temperature without damage. In the early lamps a carbon filament was used. Such lamps normally take about 4 watts per candle-power. They can be made much more efficient than that by running at a higher temperature, but the filament rapidly disintegrates and soon breaks down. The next stage was to use a filament of tungsten ; in this case the metal filament can be run at a much higher temperature and yet last a long time. Such lamps only use a little over 1 watt per candle-power. If, however, they are made to run at a still higher temperature they soon disintegrate. Disintegration can be considerably diminished by having the bulb filled with an inert gas, in which case the filament can be run at a still higher temperature. At first, however, the conduction and convection losses due to the gas more than compensated the gain of the higher temperature ; this trouble was overcome by a special arrangement of the shape of the filament which in effect diminishes the area of surface available for conduction to the gas as compared to the radiating surface. The filament is wound in a spiral of extremely small pitch. The

modern gas-filled lamp (using argon as the inert gas) only uses a trifle over  $\frac{1}{2}$  watt per candle-power.

Thus it will be seen that the problem of lamp design was to get a filament which could be run at a very high temperature and yet last a reasonable time. An ordinary carbon lamp can be made to give 1 candle-power per half-watt by over-running it (i.e. putting it on a circuit where the voltage is much greater than that for which it is designed), but in that case the filament usually lasts only a few minutes.

### Some Practical Considerations.

The properties of radiation, which have just been considered, have an important bearing on many practical problems, of which one or two may be mentioned.

**Heat Insulation.—The Thermos Flask.**—The object of the thermos flask is to prevent as far as possible the contents from losing heat to the surroundings or gaining heat from them; the original apparatus, known as a Dewar vacuum vessel, was designed chiefly for the latter purpose, and was used for containing liquid air and other liquefied gases. The vessel (Fig. 104) is double walled and the space between the walls is exhausted to a very high vacuum. This forms the best possible obstacle to the transference of heat by conduction or convection across the space. Radiation, however, travels more readily across a vacuum than when there is a material medium; advantage is therefore taken of the fact that a highly polished metallic surface is a

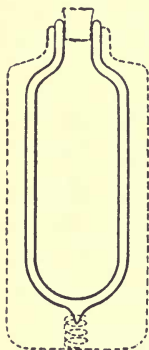


FIG. 104.

very bad radiator. The outside of the inner vessel and the inside of the outer are therefore silvered and given as bright a surface as possible; radiation from the surface of the inner vessel is thus reduced to a minimum, and very little of this small amount of radiation is absorbed by the outer vessel but most of it is reflected. In the same way radiation from the outer vessel to the inner is equally diminished.

The mouth of the flask is usually closed by a cork, so that there is a slight conduction leak here and also across the top through the glass; the latter is therefore made as thin as possible consistent with strength. These leaks are small, and the arrangement forms the most efficient heat insulator available. The flask being rather fragile, is surrounded by an outer metallic vessel, and a spring at the base and suitable soft packing are provided to protect it from shocks.

**Radiation from the Earth. Screening Action of Clouds.**—It is a matter of common observation that it is colder on a clear night than when the sky is heavily clouded. In both cases the earth is radiating; on the clear night the radiation can pass out freely, but when clouds are present they act as a screen.

Some of the radiation which falls upon the clouds is irregularly reflected back towards the earth, and the remainder is practically all absorbed since water is very adiathermanous to long wave radiation. The absorbed radiation raises the temperature of the cloud, which therefore radiates on its own account.<sup>1</sup> Some of this radiation is sent towards the earth. Thus the earth receives radiation and so the net loss of heat is less rapid than when the radiation passes away without interruption.

To a lesser extent the presence of a large amount of water vapour in the air will have an effect in reducing the rate of loss of heat; water vapour is distinctly adiathermanous, and so absorption of radiation takes place and subsequent radiation back; in a very dry climate therefore the nights tend to be colder than in a moist one.

**Selective Absorption of Glass.**—Two examples of this may be quoted. Glass is sometimes used in fire-screens; it allows the light to pass through, and also a little of the infra red radiation. It absorbs strongly all the infra red radiation below a certain wave length, and since with an ordinary fire the greater part of the total radiant energy is contained in

<sup>1</sup> See page 233. "Theory of Exchanges."

constituents of long wave length, the screen will cut out a large part of the heating effect but allow the fire to be seen.

Another example is seen in the action of an ordinary greenhouse, or any glass-roofed building. When sunlight falls upon the glass the visible portion of the radiation and the shorter wave length part of the infra red is transmitted, while the longer wave length portion of the infra red is absorbed and the glass is thereby heated. The sun is at a very high temperature (something like  $6,000^{\circ}\text{C.}$ ), and consequently a considerable portion of the total energy radiated is of short enough wave length to be transmitted.

The transmitted radiation is absorbed by the floor and objects inside the greenhouse, which become heated. When, however, they radiate, the radiation is of long wave length (since they are not nearly hot enough to begin to be luminous), and is not transmitted through the glass. The glass thus absorbs most of this radiation and radiates back to the interior, just as in the case of the cloud in the last paragraph. The effect, however, is much greater because the glass is already absorbing radiation from the sunlight as well as the radiation from the interior. It thus radiates more than it receives from the interior, and the temperature of the interior is raised. The heating of the interior is thus due to the selective absorption of glass which lets through a large part of the solar radiation but will not let through the longer wave-length radiation from the objects inside the greenhouse.



## CHAPTER XV

### LAWS OF RADIATION

**Prevost's Theory of Exchanges.**—From the foregoing account of the properties of radiation, it might be assumed, in the absence of any statement to the contrary, that a body only begins to radiate when it is at a higher temperature than its surroundings; so that if a hot body is placed in an enclosure it will radiate to the surroundings until it has reached the temperature of the enclosure and then stop. We shall find, however, that if we adopt this point of view it will be difficult to account for many observed phenomena; a much more helpful way of regarding the matter is to consider that radiation is going on all the time, and that when the hot body reaches the temperature of the enclosure it does not stop radiating, but an equilibrium is reached in which the amount of radiation given out by the body is equal to the amount it absorbs from the surroundings. This theory was proposed by Prevost to account for results of the type indicated in the next paragraph; it was developed quantitatively by Kirchoff and Balfour Stewart and has been of great importance in the theory of radiation.

If a lump of ice be brought near a thermopile, the galvanometer immediately indicates a cooling effect as if the ice were emitting a cold radiation. A more remarkable effect is observed if two large concave mirrors are placed facing one another and a thermopile is placed at the principal focus of one of them. If a piece of ice be placed at the principal focus of the other a very marked cooling effect is indicated by the galvanometer, but if the ice is shifted from this position the cooling effect is much less. The effects are precisely analogous to the heating effect observed if a hot object be substituted for the ice.

Let Fig. 105 represent an enclosure, the walls of which are maintained at some particular temperature by external means. Let a body A at a different temperature be placed in the enclosure.



Experience tells us that A will ultimately come to the same temperature as the walls of the enclosure; this might be expressed that A loses heat by radiation to the walls or gains heat by radiation from them until it attains their temperature.<sup>1</sup>

According to the Theory of Exchanges, however, the walls are radiating to A and A is radiating to the walls; the temperature of A will rise or fall according to whether the body absorbs more radiation than it emits or vice versa. When these two amounts become equal the temperature remains steady, but the radiation is regarded as still going on, so that the enclosure is crossed by streams of equal and opposite radiation. If other bodies, B, C, are placed in the enclosure, each of these attains the temperature of the walls, whether the others are present or not.

Since the presence of these other bodies does not affect the temperature attained by A wherever it may be placed in the enclosure, it follows that they do not produce any alteration in the radiation streams in the space. This means that if they absorb any part of the radiation which falls upon them they must also radiate an equal amount. This involves the condition, which we have already seen

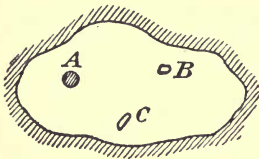


FIG. 105.

has been found by experiment, that a substance which is a good radiator is a good absorber.

For suppose A is a piece of metal with a dull black surface, B is a piece of metal with a polished surface, and C a piece of rock salt. A absorbs most of the radiation falling on it from all sides, but radiates a large amount in all directions also, so that we get our opposing streams of radiation. B reflects most of the incident radiation and absorbs very little. The reflected radiation has only to be supplemented by the small amount which a body with polished surfaces can radiate to produce the opposing streams as before. C transmits nearly all the radiation incident from all sides; the radiation from the walls on one side passes through it to the other and we get our opposing streams as before. Very little radiation from C is

<sup>1</sup> If there is any material medium in the enclosure, conduction or convection may assist in the process, but the final result would be the same if the space were vacuous.

required to restore the small amount absorbed by it from the general stream.

It follows also that not only does each body in the enclosure emit a quantity of radiation equal to that which it absorbs, but it emits radiation of the same quality also. For if it did not the quality of the radiation streams would be altered by the presence of such a body; the proportion of radiation of some particular wave length would be increased.

If then we had some substance which absorbs radiation of this particular wave length strongly and other radiation very little it would absorb more energy from the altered radiation stream than it would from the original. But what it radiates would depend only on its own nature and temperature, and so it would rise to a higher temperature than under the original conditions. This however is contrary to experience; all bodies in a constant temperature enclosure ultimately reach that temperature whether other bodies are there or not, so that the presence of these bodies does not alter the character of the radiation stream.

This connection between the quality of the radiation which a substance can absorb and that which it radiates is a well-known experimental fact, to which allusion has already been made (see footnote, page 226). Rock salt, which is very diathermanous to most kinds of radiation, absorbs strongly the radiation from a heated piece of rock salt. A piece of red glass, i.e. glass which transmits red light but absorbs strongly light of all other colours, will if heated to a high enough temperature give out light of the colours which it absorbs and appears bluish. A dull black surface which absorbs radiation of all wave lengths almost equally well (but no perfectly black surface has been produced of which this is strictly true) can radiate all wave lengths if raised to the required temperature, and so on.

**Full Radiation.**—Since the presence of various bodies in the enclosure does not alter the character of the radiation streams when temperature equilibrium has been attained, it follows that these streams must contain radiation of all wave lengths which a body at that temperature could emit; moreover the energy density (amount of energy per unit volume) for each constituent must be the maximum for that temperature. For if one of the bodies were "perfectly black" (i.e. absorbed 100 per cent. of any radiation incident upon it, whatever the wave length) the radiation from it would correspond to the general stream; the

radiation from all other bodies would merely have to make up the deficit in the general stream caused by their partial absorption. For this reason the radiation stream inside a constant temperature enclosure is spoken of as the "full" or "complete" radiation corresponding to that temperature; and if we have such a constant temperature enclosure with a small aperture through which the radiation can escape the radiation from it will correspond to the radiation from a perfect black body whose surface coincided with the aperture.<sup>1</sup> Since the objects inside a constant temperature enclosure attain the same temperature whatever the nature of the walls, it follows that the radiation stream inside is independent of the material of the walls, a fact which is borne out by experiment. The full radiation corresponding to any temperature is therefore something which is independent of the properties of any substance.

**The Theory of Exchanges.**—The Theory of Exchanges (which as we have seen starts with the idea that a body at any

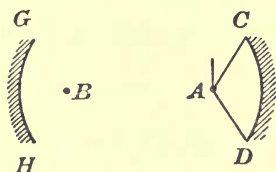


FIG. 106.

temperature is always giving out radiation, depending only on the temperature and nature of the body, and that when its condition remains unchanged it is absorbing radiation at a rate equal to that at which it is radiating) is very helpful in simplifying our ideas and enabling us to predict what will

happen in any given conditions. Let us apply it to the case mentioned on page 233.

The thermometer placed at A (Fig. 106) at the principal focus of one mirror is radiating in all directions and is receiving radiation from its surroundings (the walls of the room and other objects). Let us suppose it has taken up a constant tempera-

<sup>1</sup> In the further development of the Theory of Radiation difficulties arose which caused some doubts as to the validity of the assumption that full radiation and black body radiation are identical. These difficulties can be overcome, e.g. in Planck's theory, but some writers prefer to define full radiation as the radiation in an impervious enclosure and avoid committing themselves as to its relation to black body radiation. The discussion of these points is a good deal beyond the scope of this book; a comparatively simple account is given in N. R. Campbell's *Modern Electrical Theory*.

ture. The rate at which it absorbs radiation must then be equal to that at which it emits it. Those portions of the radiation from surrounding objects which happen to pass through B and fall on the mirror GH (B is the principal focus of GH) will suffer reflection at the two mirrors and fall on A; <sup>1</sup> the mirrors themselves as polished surfaces will radiate very little.

Thus nearly all the radiation stream which reaches A from directions between DA and CA must have passed through B. Now let a piece of ice be placed at B. A good deal of the radiation coming up to B will be absorbed by the ice which is adiabatic for long wave radiation and so will not reach A. The ice will radiate, but being at a low temperature will not radiate so much the objects in the room (assuming that the room is above 0° C.), and so the radiation reaching A by reflection at the two mirrors will be less than before. The thermometer goes on radiating, but is now receiving less than it did before, and so the absorbed radiation no longer balances that emitted and the temperature falls. Putting the ice at B enables it to intercept a larger part of the radiation streams travelling to A than it would do anywhere else (except of course if the ice were so close to A as to subtend a bigger angle than DAC), and so its effect is most marked in this position.

**Rate of Cooling of a Hot Body.**—When a body is at a higher temperature than its surroundings it will cool, and the rate of loss of heat depends on the nature of the body and on the temperature. For many purposes it is important to know what the relation is between temperature and rate of loss of heat. The earliest attempt to express this relation is due to Newton, and is known as *Newton's Law of Cooling*. This Law states that the rate of cooling of a body is proportional to the excess of its temperature above that of its surroundings. It is sometimes forgotten, however, in speaking of this law that Newton was referring to particular conditions; he was concerned with bodies placed "in a cold place where the wind blows," e.g. a draughty cellar, so that the loss of heat was mainly due to conduction and convection. Even in fairly still air, such as that of a room, the law is approximately true, if the temperature excess is not large, so that the radiation loss is a small fraction of the total loss. It

<sup>1</sup> A small fraction of it will be absorbed by the mirrors since the surface is not a perfect reflector.



is, for example, sufficiently near the truth to be used for making a correction for cooling in calorimetry if the temperature of the calorimeter does not rise more than 6 or 7 degrees above the room temperature. It is not true if the temperature excess is large, and it is certainly not true when the cooling is due to radiation only and conduction and convection are eliminated.

**Radiation Laws.**—Dulong and Petit <sup>1</sup> made a long series of experiments on the rate of cooling of large mercury-in-glass thermometers placed in an enclosure kept at constant temperature. Experiments were made both when the enclosure contained gas and when it was exhausted to the best vacuum they could obtain. By these methods the conduction effect was separated as far as possible from the radiation.<sup>2</sup> They found that the rate of cooling was not proportional to the excess of temperature, but increased more rapidly as the temperature was raised. They found that the actual value of the temperature of the thermometer and enclosure mattered; the rate of cooling when the thermometer was at say 60° C. and the enclosure at 40° C. was greater than when the thermometer was at 50° C. and the enclosure at 30° C. They found that there was a simple relation between the rate of cooling for a given excess of temperature of the thermometer over that of the enclosure and the temperature of the enclosure. From this relation a formula was deduced which was regarded as representing the radiation Law. Later experiments have shown that this formula does not satisfactorily express the relation between radiation and temperature, and the work of Dulong and Petit is of interest chiefly as the first really systematic investigation. After the time of Dulong and Petit a number of experiments were made on the rate of cooling of hot bodies and also the rate of emission of energy from a wire heated by having a current of electricity passed through it; in this case the rate of loss of energy is obtained from the strength of the current and the potential difference between its ends.

**Stefan's Law.**—In 1879 Stefan suggested that the total radiation from a body was proportional to the fourth power of its absolute temperature. He was led to this idea by considering

<sup>1</sup> *Ann. de Chimie et de Physique*, 2<sup>e</sup> Ser., tom. VII, 1817.

<sup>2</sup> Strictly speaking, the effect of the gas is not confined to conduction and convection. The rate of radiation is somewhat influenced by the medium. Cp. Balfour Stewart's *Heat* or Poynting and Thomson's *Heat*.



the results of an experiment of Tyndall's on the rate of emission from a platinum wire. He also examined the results of Dulong and Petit from the point of view of this law and found that they agreed with it very well; better in fact than with the law given in their paper. It is worth while considering precisely what is meant by this fourth power law.

If we have a body of which the area of surface is  $A$  sq. cm. and the temperature is  $\theta^\circ$  C., the energy radiated per second is

$$A\sigma(\theta + 273)^4,$$

where  $\sigma$  is a constant depending on the nature of the surface. But at the same time it is absorbing radiations from its surroundings and so the nett loss of energy is the difference between what it radiates and what it absorbs. Suppose that it is placed in an enclosure at  $15^\circ$  C. When the body is at  $15^\circ$  C. its temperature remains constant. It must therefore absorb as much from the enclosure as it radiates. But at  $15^\circ$  C. the energy it radiates per second is

$$A\sigma(15 + 273)^4$$

and this must also represent what it absorbs from the radiation of the enclosure.

When it is at  $\theta^\circ$  C. the nett rate of loss of energy by radiation must be <sup>1</sup>

$$A\sigma(\theta + 273)^4 - A\sigma(15 + 273)^4.$$

It is instructive to take a numerical example. Let us compare the rate of loss of heat by radiation for a body when its temperatures are respectively  $1,000^\circ$  C. and  $500^\circ$  C. and the enclosure is at  $15^\circ$  C.

In the first case the loss is  $A\sigma(1273)^4 - (288)^4$ .

In the second case the loss is  $A\sigma(773)^4 - (288)^4$ .

The ratio of these is  $\frac{(1273)^4 - (288)^4}{(773)^4 - (288)^4}$ , since  $A\sigma$  is the same for each.

This is equal to  $\frac{2625 \times 10^9 - 6.88 \times 10^9}{357.2 \times 10^9 - 6.88 \times 10^9} = \frac{2618}{350.3} = 7.45$ .

<sup>1</sup> This assumes that the absorptive power of the body for the radiation from the enclosure does not depend on the temperature of the body. There is some ground for supposing this; but as we shall see later Stefan's Law is only strictly true for a perfect black body, and such a body by definition absorbs 100 per cent. of all radiation which falls on it whatever the temperature, in which case of course our condition is satisfied.

Thus doubling the temperature has increased the radiation nearly  $7\frac{1}{2}$  times.

With Stefan's Law we get for the first time the relation between radiation and temperature on a satisfactory basis. Nevertheless the results of some observers are not in accordance with this law, and it is important to realize in what the value of the law consists and also the conditions in which it does not apply.

Boltzmann showed that the law could be deduced from considerations of thermodynamics and the electro-magnetic theory of light in the case of full radiation for an enclosure. A number of experiments have been made to verify the law, of which the work of Lummer and Pringsheim<sup>1</sup> is the classical example. Using for the radiator an enclosure kept at a constant temperature and provided with a small aperture, they measured the radiation with a surface bolometer at different distances and found that the law was well obeyed over a very wide range. It may therefore be regarded as established that the law holds for full radiation, and therefore in the case of a body which approximates to a perfectly black body the law represents sufficiently closely what happens. When, however, we are dealing with bodies which do not approximate to black bodies considerable departures may arise, especially in the case of those substances which show well-marked selective absorption.

**Radiation Laws concerned with the Distribution of Energy in the Spectrum.**—It has already been stated (page 227) that if the spectrum of a hot body were explored with a bolometer the energy is a maximum for some particular wave length depending on the temperature. Formulæ have been deduced from theoretical reasoning for the distribution of energy in the case of full radiation.

These formulæ may be referred to here.

If  $\lambda_m$  is the wave-length corresponding to the position of maximum energy in the full radiation for a temperature  $\theta^\circ$  (Absolute), then

$$\lambda_m \theta = \text{constant (Wien's Displacement Law).}$$

The emissive power for the wave length of maximum energy is proportional to the fifth power of the absolute temperature.

Lastly, a formula giving the emissive power for any particular

<sup>1</sup> *Ann. der Physik*, Bd. LXIII. 1897. A good account is given in Preston's *Theory of Heat*, Third Edition.

wave length has been deduced by Planck. These formulæ only apply to full radiation ; they do not apply in the case of a body which is not perfectly black.

An elaborate series of experiments were made by Lummer and Pringsheim to test the truth of these formulæ, using a constant temperature enclosure as the source of radiation. The results showed in all cases a very good agreement between observed values and those given by the theory. The discussion of these formulæ is beyond the scope of this book.

The chief point is to realize that they have been deduced and that together with Stefan's formula they have been found to represent the facts for full radiation. They are of importance in the determination of temperatures by radiation as described in the next chapter.

## CHAPTER XVI

### ON THE MEASUREMENT OF TEMPERATURE IN INDUSTRIAL AND OTHER PROCESSES

**Expansion-of-liquid Methods.**—The ordinary mercury-in-glass thermometer is an example of the use of expansion-of-liquid method, but such an instrument is in many ways unsuited for industrial processes. What is required is a quick-acting instrument not likely to be damaged by moderately rough usage, and in a number of cases it is desirable to have the indicator at some distance away from the place where the temperature is being measured.

A very useful form, suitable for temperatures up to  $540^{\circ}\text{C}$ . ( $1,000^{\circ}\text{F}$ .), is the steel-bulb mercury thermometer (Fig. 107). A steel bulb is connected by flexible steel capillary tubing to a flat steel tube coiled in a spiral and forming the Bourdon tube of a dial gauge. The system of bulb, capillary tube and Bourdon tube is completely filled with mercury under pressure. When the bulb is heated the mercury expands and this tends to uncoil the Bourdon tube and so moves a pointer over the dial of the gauge. The latter is graduated to show degrees, and by having a suitable length of capillary tube the dial can be placed at any convenient place away from the source of heat.

Such instruments are suitable for temperatures between  $-40^{\circ}\text{C}$ . (the freezing-point of mercury) and  $540^{\circ}\text{C}$ .; the mercury, completely filling the system and being under pressure, is not able to boil. Above  $540^{\circ}\text{C}$ . mercury begins to attack the steel and incidentally the pressure developed at this temperature is very large.

There is a slight error due to the uncertain temperature

of the mercury in the capillary tube, and for this reason 75 feet is usually quoted as the maximum length of tubing permissible. In the pattern produced by Messrs. Negretti and Zambra, the error due to changes in temperature of the capillary tube is overcome by an ingenious compensating device. The capillary tube is made of high-expansion material and has running throughout its length a wire of low-expansion material (invar), slightly smaller in diameter than the bore of the tube. The wire is cut into lengths so that it can slide in the tube when the temperature changes. The mercury occupies the annular space between the tube and the wire; by suitably adjusting the diameter of the wire it can be arranged that the expansion of the tube just equals the expansion of the small volume of mercury in the annular space, and so the mercury in the tube just fills its available space whatever the temperature of the latter, and so the indications on the gauge are not appreciably affected by variations in the temperature of the tube.

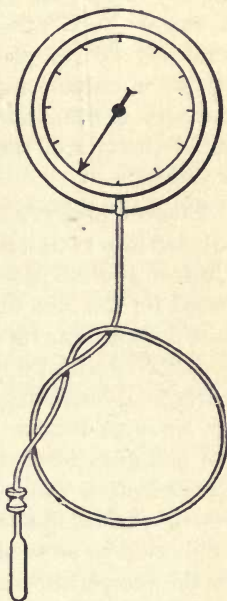


FIG. 107.

#### Vapour Pressure Thermometers.

—In these instruments advantage is taken of the fact that the pressure of the vapour of any substance in contact with the liquid (saturation pressure) depends only on the temperature and not on the volume of the container. In appearance the thermometer, which was developed by J. B. Fournier, is somewhat similar to the steel-bulb thermometer mentioned in the preceding paragraph. The bulb contains the liquid and its saturated vapour, and the pressure is transmitted through the capillary tube to a pressure gauge graduated to read degrees. It will be obvious that changes in the volume of the bulb or capillary tube



will not affect the reading of the pressure, and the gauge can be at any distance. As the vapour pressure of a liquid increases very rapidly with temperature, it is not satisfactory to attempt to use the same instrument to cover a very wide range of temperature; separate thermometers are made in a variety of ranges. Thus one instrument might be used for a range  $-25^{\circ}$  to  $+25^{\circ}$  C., another  $180^{\circ}$  C. to  $340^{\circ}$  C., another  $500^{\circ}$  to  $850^{\circ}$ . They can be used for temperatures up to a value considerably above that of the steel-bulb mercury thermometer. A type is also made to show clearly small changes of temperature between two limits not widely separated.

**Electrical Pyrometers.**—Electrical pyrometers may be divided into two classes: resistance thermometers and thermo-electric thermometers. The action of the former class is based on the fact that the electrical resistance of a platinum wire increases as its temperature is raised. The thermometer consists essentially of a coil of fine platinum wire wound on a frame of insulating material <sup>1</sup> and having its ends connected by leads to terminals. The whole is protected from injury by being enclosed in a tube of porcelain or quartz. The instrument is connected to some form of Wheatstone bridge which enables its resistance to be measured: the bridge is calibrated so as to show the temperature directly. A change in the temperature of the leads and connections would cause a change in their resistance and hence an error in the resulting observation; thermometers for accurate work are made with a second pair of dummy leads side by side with the leads of the coil, and these are connected to the bridge by wires similar to those connecting the real leads. The bridge is arranged to measure the difference between the resistance of the coil + its leads and that of the dummy leads. Thus, any changes in resistance of the leads are automatically compensated and the resistance of the coil only is measured.

<sup>1</sup> The most suitable material appears to be mica, but some forms of successful industrial instruments are wound on quartz.

Of the special types of bridge for this work the two best known are the Callendar Recorder and the Whipple Indicator: the scale of the latter is calibrated to indicate single degrees from  $-10^{\circ}\text{C.}$  to  $1,200^{\circ}\text{C.}$  For some types of industrial work the use of dummy leads can be dispensed with and the indicator calibrated to read sufficiently accurately. Platinum resistance thermometers can be used over a very wide range of temperature; they can be used for low temperatures such as  $-200^{\circ}\text{C.}$  and can also be employed for temperatures up to about  $1,400^{\circ}\text{C.}$  The upper limit of temperature is fixed by the fact that no material for the protecting tube has yet been found which is capable of satisfactorily withstanding higher temperatures than about  $1,400^{\circ}\text{C.}$

The two most important points in the design of these instruments are efficient insulation and the avoidance of mechanical strain in the coil; the latter would cause a change in resistance so that the instrument would be inconsistent, i.e. would not always give the same indication for the same temperature.

**Thermo-electric Pyrometers.**—These instruments, like the thermopile, depend on the fact that if we have a circuit of two different metals and one junction is heated, a current of electricity tends to flow round the circuit. The electromotive force depends on the kind of metals used and on the difference in temperature between the hot junction and the cold. The apparatus consists of the "thermo-couple" (two dissimilar metals joined at one end), which is connected to an indicator which is some form of galvanometer calibrated to read the temperature direct. The wires of the thermo-couple are protected by a tube as in the case of the platinum resistance thermometer.<sup>1</sup>

For temperatures up to  $1,400^{\circ}\text{C.}$  the most suitable materials

<sup>1</sup> This is for general and industrial use. In the case of laboratory use there are occasions when it is better to use a thermo-couple not enclosed in a tube, and it may also be better to use a potentiometer instead of the galvanometer.

for the thermo-couple are platinum and an alloy consisting of platinum with 10 per cent. of rhodium.

For temperatures up to about 600 or 700° C. other metals can be used and in some respects are more suitable; a very common pair is formed of iron and the alloy constantan. (For industrial purposes thermo-couples are classified as "rare-metal" and "base-metal" respectively.)

As already mentioned, the indication of the galvanometer depends on the difference in temperature between the hot junction and the cold junction. If ordinary wire leads are used to connect the thermo-couple to the indicator, the "cold junction" will be in effect where these leads join the thermo-couple, and this may be affected by the source of heat. If, however, the two ends of the thermo-couple are connected by leads of the same material as the materials of the thermo-couple itself, the cold junction is transferred to the galvanometer, which is some distance away and not likely to be affected by the source.<sup>1</sup> This is usually done in the case of the iron-constantan couples, but in the case of the rare-metal couple it would be very expensive to have long leads of platinum and platinum-rhodium. The difficulty can be got over by using "Peake's compensated leads," which are wires of inexpensive alloys chosen to give the same electromotive force as the platinum—platinum-rhodium. The compensation cannot be made quite exact for all temperatures.

Thermo-electric pyrometers are on the whole less accurate than resistance thermometers, but are more convenient to use and are more adapted to industrial purposes. They can be used for rather higher temperatures than platinum resistance thermometers and can also be used for low temperatures.

**Radiation Pyrometers.**—In many cases it is not desirable or even possible to have an instrument in actual contact with the hot body; and for temperatures over 1,500° C. none of the above pyrometers is suitable. In such cases radiation

<sup>1</sup> Another, and more accurate, method, is to have the cold junction in a Dewar vacuum vessel which keeps its temperature remarkably constant.

pyrometers are used. These instruments make use of the laws of radiation mentioned on page 241. Most of those used in practice belong to one or other of two types.

In the one type the intensity of the total radiation is measured, and the calibration is based on Stefan's Law. In the other the intensity of the radiation of some particular wave length is measured or rather compared with that from a standard source; as this comparison is carried out by optical methods it cannot be used for temperatures below about  $700^{\circ}\text{C}$ ., i.e. "dull red heat," whereas the total-radiation type

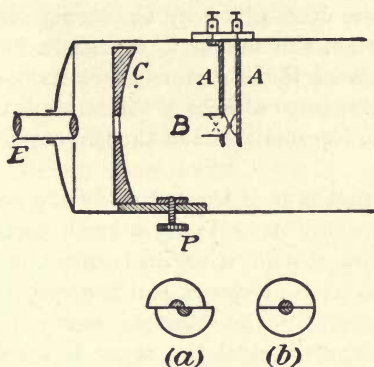


FIG. 108.

can be used for temperatures as low as  $500^{\circ}\text{C}$ . There is no upper limit to the temperature which radiation instruments are capable of measuring.

The best-known instrument of the first type is the Féry radiation pyrometer (Fig. 108). It is made up of a short tube open at one end directed towards the hot object. At a point on the axis of this tube is a small iron-constantan thermo-couple, the two wires of which are connected to terminals on the outside through two metal strips A A. The radiation is focussed on to the thermo-couple by a concave mirror C, which can be moved by a pinion P. In order to see whether the focussing is correct an eyepiece E is provided,

and one of the strips A carries a short tube B in which are two semicircular plane mirrors inclined at a small angle to one another and with an opening at the axis of the tube through which the radiation passes. If the radiation is not correctly focussed, the general appearance on looking through the eyepiece is as in Fig. 108 (a); the pinion is turned until the appearance is as in Fig. 108 (b). The electromotive force generated in the thermo-couple is indicated by a galvanometer connected to the terminals. The tube B and its mirrors screen off some of the reflected radiation from the thermo-couple; the rays which do reach it form a cone of which the angle is determined by the arrangement of B and is not altered when the mirror is moved in focussing.

The indications of the instrument are independent of its distance from the source of heat if the latter is not too great. This follows from the small area of the thermo-couple exposed to radiation.

If the instrument is near the hot body the concave mirror forms a large image of it, and only a small part of the image covers the thermo-couple; if the instrument is further away the image is smaller and consequently a larger part of it is on the thermo-couple. The effect of distance is thus automatically compensated until the stage is reached that the image is so small that the whole of it is on the thermo-couple; beyond this distance the indications of the galvanometer would fall off.<sup>1</sup>

In the case of instruments of the second type, the radiation of some particular colour is matched against light of the same colour from a standardized electric lamp. These instruments are usually classified under the heading of "optical pyrometers." Several very good optical pyrometers are obtainable, of which we may take the "disappearing filament" type as an example.

<sup>1</sup> Another instrument of this type, the Foster-fixed focus pyrometer, has a diaphragm near the open end of the tube, and the mirror is arranged so that the diaphragm and the thermo-couple are at conjugate foci. In this case no focussing is needed.



The hot object is viewed through a species of telescope, the eyepiece of which is fitted with a piece of glass which transmits only light of one colour, usually red. Inside the telescope is a small electric lamp; the position of which is adjusted so that the filament is in the same plane as the image of the hot body formed by the object glass. Thus, on looking through the eyepiece the image of the hot body appears superposed on the filament. The current through the lamp is varied until the filament just disappears; this means that as far as the light of the one colour is concerned, the brightness of the filament and image are the same.

Thus, the temperature of the filament corresponds to that represented by the image, and the current indicator of the lamp is calibrated to show directly the temperature of the hot body. As in the case of the other kind of radiation instrument, the readings are independent of the distance of the hot body within wide limits.

**The Meaning of the Temperature indicated by Radiation Pyrometers.**—It was explained on page 241 that the various radiation formulæ, such as Stefan's, Planck's, etc., apply only to the case of full radiation or the radiation from a perfect black body. In the case of bodies which are not black no very satisfactory quantitative laws are obtainable; it is obvious also that if they were we should have a different set of values for each surface. Radiation pyrometers are therefore calibrated on the basis of full radiation and they give what is known as the "black body temperature" of an object, i.e. the temperature of a perfectly black body which would give the same value of radiation as the actual body. Fortunately, however, in many of the cases for which radiation pyrometers are used the conditions approximate fairly closely to those of a black body. For example, the case of a furnace where the radiation is observed through a small opening in the door; an ingot of metal actually in a furnace (where it is required to heat the metal to a particular temperature before withdrawing it for the next process), or a muffle at a uniform temperature all give practically full

radiation. Again, metals which when heated become tarnished with a black oxide approximate to a black body.

On the other hand, if the pyrometer is sighted on a body not in an enclosure and having a highly reflecting surface, the "black body" temperature recorded will be considerably lower than the actual temperature. All that the pyrometer tells us then is that the temperature of the body is certainly not lower than a particular value.

It may be mentioned that the radiation from a body with a reflecting surface is in general less deficient in the regions of short wave length than in those of the long; consequently, the temperature given by an optical pyrometer is likely to be nearer the truth than that given by a total-radiation pyrometer.<sup>1</sup>

**Temperature of the Sun.**—By making use of the radiation laws it is possible to obtain an estimate of the temperature

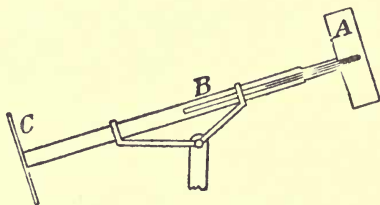


FIG. 109.

of the sun. The greater number of determinations are based on total radiation. First of all the amount of energy radiated in unit time on a given area of the earth's surface is determined. The apparatus used for this purpose is known as a pyroheliometer. In its earliest form (that due to Pouillet) this is simply a thin copper calorimeter, blackened on the surface facing the sun and silvered on the remaining surfaces. The calorimeter A (Fig. 109) was mounted on an axle B,

<sup>1</sup> Standard books on temperature measurement are Ezer Griffith's *Methods of Measuring Temperature* (Griffin, 1918) and the somewhat older *The Measurement of High Temperatures*, Burgess and Le Châtelier. A very complete account (also by Griffiths) of pyrometers is

on the other end of which was a disc C. By moving the axle so that the shadow of A just covered the disc, it could be arranged that the sun's radiation fell perpendicularly on the blackened face of A. The rate of rise in temperature of the contents of the calorimeter was noted and also the rate of cooling when the apparatus was screened from the sunshine. Knowing the thermal capacity of the calorimeter and contents and allowing for the cooling, the radiation energy falling per minute on the end of A was calculated. This is not a very satisfactory method, and a much better form was used by Abbot and Fowle in 1909 (Smithsonian Reports or Preston's *Theory of Heat*). Allowance has then to be made for absorption in the atmosphere. This is difficult, as the absorption is different for different wave lengths and is also very much dependent on the amount of water vapour in the atmosphere. It may be estimated by comparing the radiation received when the sun is nearly overhead and when it is near the horizon so that the radiation traverses a greater thickness of the atmosphere; also by comparing the effects at stations of different elevation.<sup>1</sup>

Many determinations have been made in this and other ways, and the values generally regarded as trustworthy range from 2 to 2.5 calories per minute on each square cm. of the earth's surface after allowing for absorption in the atmosphere. We will assume a mean value 2.3 calories per minute and obtain a value for the sun's temperature. Taking the mean

given in the *Dictionary of Applied Physics*, Vol. I. (Macmillan). Féry's original instrument is described in *Comptes Rendus*, Vol. 134, p. 977 (1902). Preston's *Theory of Heat* has a good account of the subject. Much information is to be got from makers' lists, especially those of the Cambridge and Paul Instrument Company. The lists of Fournier et Cie of Paris give vapour-pressure instruments, and Negretti and Zambra the compensated steel-bulb mercury thermometer. Griffin's catalogue has a good deal about resistance thermometers and thermocouples. Reference may also be made to a paper by R. S. Whipple on "Modern Methods of Measuring Temperature," *Proceedings of the Institution of Mechanical Engineers*, July, 1913; and to the ever-useful table of Physical Constants of Kaye and Laby.

<sup>1</sup> Langley, *Researches on Solar Heat*, 1884. *Phil. Mag.*, 1883. Langley and Abbot, Smithsonian Reports, 1903 and later.

distance of the earth from the sun as 93,000,000 miles and assuming that the sun is radiating equally in all directions, this means that each sq. cm. on a sphere of radius 93,000,000 miles is receiving energy at the rate of 2.3 calories per minute. The energy radiated from the surface of the sun per minute must be equal to the energy falling per minute on the surface of any sphere which surrounds it. Thus the energy radiated from each square cm. of the sun's surface must be—

$$\frac{2.3 \times \text{area of surface of a sphere of 93,000,000 miles radius}}{\text{Area of the sun's surface}}$$

calories per minute.

Taking the sun's radius as 430,000 miles, this is—

$$\frac{2.3 \times 4\pi \times (93,000,000)^2}{4\pi \times (430,000)^2} = \frac{2.3 \times (9.3)^2 \times 10^{14}}{(4.3)^2 \times 10^{10}} \text{ calories per minute}$$

$$= \frac{2.3 \times (9.3)^2 \times 10^{14}}{(4.3)^2 \times 10^{11} \times 6} \text{ calories per second.}$$

Now by Stefan's Law the energy radiated by a black body is—

$$A\sigma\theta^4 \text{ or } \sigma\theta^4 \text{ per unit area.}$$

$\sigma$  has been determined by experiments of the kind performed by Lummer and Pringheim (page 240). The recent determination by Millikan (1917) gives  $\sigma$  as  $5.7 \times 10^{-5}$  ergs per second. Taking 1 calorie as  $4.2 \times 10^7$  ergs, we have—

$$\frac{2.3 \times (9.3)^2 \times 4.2 \times 10^{21}}{(4.3)^2 \times 6 \times 5.7 \times 10^6} = \theta^4 \text{ where } \theta \text{ is the black-body temperature of the sun.}$$

$$\theta = 6,003^\circ \text{ A.}$$

Thus the black-body temperature of the sun is  $6,000^\circ \text{ A.}$  or  $5,730^\circ \text{ C.}$

It should be noticed that this is the black-body temperature; the actual mean temperature would probably be somewhat higher. Most of the recent determinations of the radiation energy received at the earth's surface are nearer to 2 calories per minute.

Other estimates of the sun's temperature are based on the distribution of energy in the spectrum.

The general conclusion to be drawn from the various experiments is that the black-body temperature of the sun



is somewhere between  $5,500^{\circ}$  and  $6,000^{\circ}$  Absolute, probably nearer the latter.

**Calibration of Pyrometers—Meaning of a Scale of Temperature.**—It is important to realize what is meant by a scale of temperature and to what extent a temperature measurement is reliable; it is particularly important in the case of high temperatures. When we speak of a temperature of  $0^{\circ}$  C. or of  $100^{\circ}$  C. the meaning is perfectly clear; we mean the temperature at which pure ice melts or the temperature at which the vapour pressure of pure water is one standard atmosphere.

But the statement that the temperature of a substance is  $50^{\circ}$  C. or  $150^{\circ}$  C. has no such definite meaning.

In fixing our scale of temperature we take some particular substance (e.g. mercury in a glass container), find out how much some arbitrary property, such as its volume, changes when the temperature is raised from  $0^{\circ}$  C. to  $100^{\circ}$  C. and divide that change into 100 equal parts; a rise in temperature of  $1^{\circ}$  is then defined as such a change of temperature as will bring about a change equal to one of these parts.  $50^{\circ}$  C. then means such a temperature that when the particular substance is heated from the melting-point of ice to that temperature, the expansion is half what it would be if it were heated from the melting-point of ice to the boiling-point of water under standard pressure.

It does not follow that the scale of temperature defined in terms of one substance will agree with a scale defined in terms of another (except, of course, at  $0^{\circ}$  C. and  $100^{\circ}$  C.); and in fact they do differ. In the case of a number of suitable substances such as mercury,<sup>1</sup> alcohol, or a gas, the scales of temperature do not differ among themselves by very much between  $0^{\circ}$  and  $100^{\circ}$  C., but at high temperatures (alcohol is not available) the difference may be a matter of several degrees. In the case of the not easily liquefiable gases such as hydrogen

<sup>1</sup> It is clear that a substance such as water, which can have the same volume at two different temperatures, is unsuitable for a thermometric substance



or nitrogen, especially if the temperature be defined in terms of the change in pressure at constant volume, the agreement between the scales is found to be very close;<sup>1</sup> these gases are therefore very suitable for thermometric substances. They have the further advantages that they can be used over a very wide range of temperature and the actual change in pressure per degree is relatively large.

In practice, therefore, the hydrogen scale or the nitrogen scale are taken as the basis of temperature measurement; other instruments, such as mercury thermometers, thermocouples, or platinum resistance thermometers, are standardized by comparison with a constant volume hydrogen thermometer or a constant volume nitrogen thermometer. From a theoretical standpoint the hydrogen thermometer is the better; but at high temperatures trouble is experienced owing to diffusion of hydrogen through the walls of the bulb. For an accurate standard the bulb should be of metal and is usually of platinum or platinum iridium; at temperatures above 400° C. hydrogen diffuses through this, so that for high temperatures a nitrogen thermometer is used. For very low temperatures and for temperatures up to 400° C. the constant volume hydrogen thermometer is the basis of temperature measurements; above this temperature the constant volume nitrogen thermometer is the basis, and accurate standardizations have been carried out with it for temperatures up to 1,600° C.<sup>2</sup>

When temperatures are measured with various instruments they can all be expressed in terms of the hydrogen scale or the nitrogen scale if they are not above 1,600° C.; such temperatures have a definite meaning apart from the particular instrument used to measure them. But when we come to measure temperatures such as 2,000° C. with some

<sup>1</sup> Observe that this is not taking the  $\beta$  coefficient as the same for each gas, but finding the actual pressure at 0° C. and 100° C. in any given case and taking 1° as the rise in temperature required to produce  $\frac{1}{100}$  of the above change in pressure.

<sup>2</sup> Cp. Swann, Carnegie Institute Publications.

form of radiation pyrometer, the result means that we have determined the behaviour of the pyrometer at temperatures below  $1,600^{\circ}\text{C}$ . and assume the law to hold for higher temperatures. Such temperatures cannot therefore have the same definite meaning as the others; the measurements of the same temperature by different types of pyrometers may differ by a matter of a few degrees.<sup>1</sup>

Finally, it may be pointed out that there is a theoretical scale of temperature—the absolute thermodynamic scale (Chapter XXI)—which does not depend on the properties of any substances. Equations have been reduced, based on the porous plug effect, which enable relations to be expressed between temperatures on either hydrogen or nitrogen scale and temperatures on this thermodynamic scale.

<sup>1</sup> Much information on this subject is given in Ezer Griffith's book, which has already been mentioned. References to original papers will be found in it. See also *Dictionary of Applied Physics*.



## PART II

### CHAPTER XVII

#### THE PROPERTIES OF GASES

In Chapter VI it was stated that Boyle's Law was not strictly true for any gas, especially at high pressures; it was further pointed out that some gases obeyed the law much more nearly than others. A rather more detailed study of this departure from the Law will throw a good deal of light on the properties of gases.

The deviation is very marked in the case of the gas sulphur dioxide; so much so that it may readily be illustrated by a simple experiment. A and B (Fig. 110) represent two tubes, closed at the top by taps, and joined at their lower ends where they are connected by a long piece of rubber tubing with a mercury reservoir C which can be raised or lowered. B is filled with sulphur dioxide and A with air; the quantity of air is adjusted so that when the level of the mercury in B and C is the same, the mercury in A comes to the same height. Thus at the start the air and sulphur dioxide are at the same pressure. The reservoir C is then gradually raised so that the gases are compressed. So long as the pressure is not much above the atmosphere the mercury in A and B rises about the same amount, but as C is raised further the mercury in B rises above that in A, showing that the sulphur dioxide is more compressible than the air. The difference becomes more marked until a stage is reached when the pressure is something over 2 atmospheres (if the room is fairly cold—at

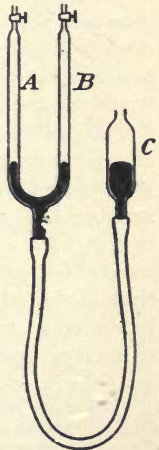


FIG. 110.

reservoir C is raised further the mercury in B rises above that in A, showing that the sulphur dioxide is more compressible than the air. The difference becomes more marked until a stage is reached when the pressure is something over 2 atmospheres (if the room is fairly cold—at



0° C., a pressure of just over  $1\frac{1}{2}$  atmospheres would suffice), at which there is a quick rise of the mercury in B and the sulphur dioxide condenses to a liquid.

Other gases, such as chlorine or carbon dioxide, behave in a similar way, but in their case a much greater pressure is required to produce liquefaction; an apparatus of the type shown in Fig. 110 would not be very suitable for showing this effect (apart from the fact that chlorine has a chemical action on mercury) as the reservoir C would have to be raised to inconvenient heights to obtain sufficient pressure to bring about liquefaction. Nevertheless the general effect is the same, i.e. as the pressure is raised the gas becomes more compressible than it would be if it obeyed Boyle's Law (so that the product  $pv$  instead of remaining constant becomes smaller), and when a certain pressure is reached, depending on the nature of the gas and its temperature, the gas begins to liquefy, and if the pressure is maintained at this value the whole of the gas turns to liquid.<sup>1</sup>

On the other hand no such effect is found with gases like air, nitrogen or oxygen. Careful experiments show that they do deviate slightly from Boyle's Law; Regnault showed that at high pressures they do become slightly more compressible than they would be according to Boyle's Law, i.e.  $pv$  diminishes.

The process, however, does not continue indefinitely; a series of experiments by Amagat<sup>2</sup> showed that as the pressure increases the product  $pv$  at first diminishes, but that at still higher pressures  $pv$  begins to increase again and reaches a value greater than it was at the beginning. In the case of hydrogen the experiments of Regnault and the later experiments of Amagat showed that the product  $pv$  increased from the start as the pressure increased; there was no initial stage when the gas was more compressible than Boyle's Law would indicate.<sup>3</sup>

<sup>1</sup> Accurate experiments show that the pressure has to be raised slightly above that at which liquefaction commences in order to complete the process. This slight increase has an important bearing on the theory of the subject.

<sup>2</sup> Amagat, *Ann. de Chimie et de Physique*, 1881.

<sup>3</sup> Casual inspection of the reproductions of Amagat's diagrams sometimes produces rather exaggerated ideas of the magnitude of these effects. As a rough indication the following figures may be quoted. At 15° C. or 16° C. increasing the pressure from 1 to 25 atmospheres would produce a decrease in the value of  $pv$  of well under 1 per cent. for nitrogen, about 1 per cent. for air, something like 25 per



Thus at first sight there appears to be a fundamental difference between a gas like carbon dioxide and a gas like nitrogen. But the meaning of this difference becomes clearer when the effect of temperature is considered. It is found that the pressure necessary to liquefy any particular gas increases as the temperature is raised, and that when the temperature exceeds a certain value, known as the critical temperature of the gas, it is impossible to bring about liquefaction however great a pressure is applied. This point may be well illustrated by considering the classical experiments performed by Andrews<sup>1</sup> with carbon dioxide. These consisted in observing the changes in volume of the gas as the pressure is increased, and repeating the operation with the gas maintained at temperatures which were successively increased.

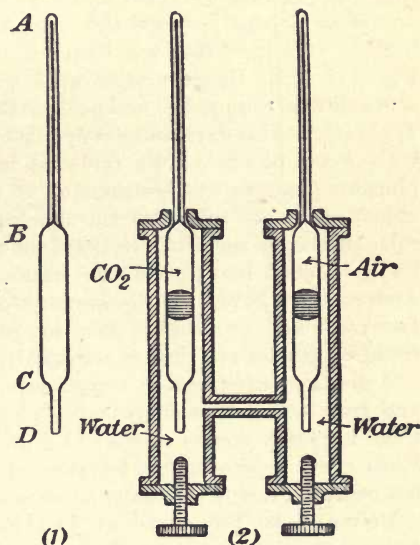


FIG. 111.

The gas was contained in a glass tube of the form shown in Fig. 111

(1). The part AB was of capillary bore, BC was about  $2\frac{1}{2}$  mm. bore and CD half this. The bore of AB was calibrated by introducing a thread of mercury and measuring its length at different positions and weighing the mercury so introduced. At the beginning both ends of the tube were open, and carbon

cent. for  $\text{CO}_2$ , and an increase of about 1 per cent. for hydrogen. At 60 atmospheres  $pv$  for nitrogen would have passed its minimum value (1 per cent. decrease) and would be increasing, for air it would have decreased about 2 per cent. and  $\text{CO}_2$  would have liquefied. At 300 atmospheres the value of  $pv$  for nitrogen would be about 20 per cent. above its original value, but the density of the gas would be comparable with that of a liquid, being something like .3 gm. per c.c.

<sup>1</sup> *Phil. Trans.*, 1869.

dioxide was drawn through for a considerable time to get rid of residual air,<sup>1</sup> the end A was sealed off and D closed ; D was then placed under mercury and opened. By gently warming the tube some of the gas escaped, and on cooling mercury entered the tube. The final quantity of gas was adjusted by placing the tube (with its end still under mercury) under the receiver of an air pump and reducing the pressure until such an amount of gas escaped that on restoring the pressure the mercury entered to the desired height. The glass tube was then enclosed in a stout copper tube, Fig. 111 (2) ; this communicated with a similar copper tube containing a glass vessel similar to ABCD (1) but containing air. The copper tubes were completely filled with water and were fitted with screw plungers ; by screwing in either or both of these plungers pressure was transmitted to the two glass tubes. The object of the air tube was to measure the pressure, which was calculated from the compression of the air. At that time Amagat had not made his experiments, and so the pressures quoted by Andrews are based on the assumption that air obeys Boyle's Law ; he had no reliable data for any correction. The gases could be kept at any desired temperature by means of a jacket.

A series of experiments were made at different temperatures and from the results curves were plotted. The general form of these curves is shown in Fig. 112, which is not drawn to scale. Each curve represents the behaviour of the gas at one particular temperature, and is spoken of as an isothermal curve.

Referring to the curve at  $13.1^{\circ}\text{C}$ . represented by ABCD. From A to B the volume of the gas diminishes as the pressure increases, and the general form of the curve is not dissimilar to the corresponding curve for air at  $13.1^{\circ}\text{C}$ ., except that the value of  $pv$  is less than for air. When the pressure reaches the value represented by B (about 49 atmospheres) liquefaction begins and continues without increase of pressure until all the gas is liquefied,<sup>2</sup> a state represented by C. The liquid being much less compressible than gas, the curve rises steeply to D, a large increase of pressure producing small changes of volume. Nevertheless the

<sup>1</sup> In spite of these precautions traces of air remained which had some effect on the results.

<sup>2</sup> Strictly speaking, it was found that BC was not parallel to the volume axis, an extra pressure of about  $\frac{1}{4}$  atmosphere being required to complete the liquefaction. This effect was largely due to residual air already referred to.

liquid in the neighbourhood of C is much more compressible than ordinary liquids. In the next curve, corresponding to  $21.5^\circ$ , a much higher pressure is reached before liquefaction begins, and the horizontal portion is shorter than CB. The gas being compressed to a smaller volume before liquefying,<sup>1</sup> there is less change in volume in passing to the liquid; moreover the liquid at  $21.5^\circ$  C. occupies a perceptibly larger volume than the liquid at

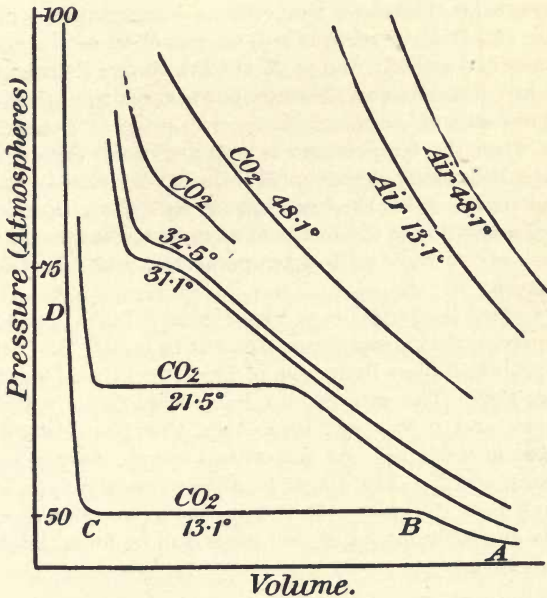


FIG. 112.

$13.1^\circ$  C.; the coefficient of expansion of liquid  $\text{CO}_2$  at pressure just enough to keep it liquid is very large.

As the temperature is raised the change in volume in passing from gas to liquid becomes smaller, the horizontal portion of the curve becoming shorter. At a sufficiently high temperature the horizontal portion vanishes altogether; this is represented by the curve for  $31.1^\circ$ . There is no stage at which decrease in

<sup>1</sup> It must be remembered that the curves refer to the same mass of  $\text{CO}_2$  in every case.

volume occurs while the pressure remains stationary; all that happens is that there is a change in the steepness of the curve, but it does not become parallel to the volume axis. It was found that there was no formation of liquid; no separation was noticed, and the appearance of the gas did not change. There is a rapid change in density at this point but no separation. Repeated experiments showed that the highest temperature at which it was possible to get the  $\text{CO}_2$  visibly to form liquid was  $30.92^\circ \text{C}$ . This temperature is therefore the critical temperature for carbon dioxide. At  $32.5^\circ \text{C}$ . there is still an inflection of the curve, but it becomes less marked, and at  $48.1^\circ \text{C}$ . the curve shows no abrupt change in volume at any pressure, but is similar in appearance to the corresponding curve for air.

Thus when the temperature is well above the critical temperature the behaviour of carbon dioxide is very similar to that of air or nitrogen. This at once suggests that the properties of air or nitrogen are due to the fact that at ordinary temperatures they are much above their critical temperatures, and this is found to be the case.

The critical temperature of nitrogen is  $-146^\circ \text{C}$ ., and so it is not surprising that it was found difficult to liquefy it. Still more difficult is it to liquefy hydrogen, of which the critical temperature is  $-234.5^\circ \text{C}$ . The gas helium long resisted all attempts to liquefy it, and it was not until 1908 that Kamerlingh Onnes succeeded in doing so. As the critical temperature of helium is somewhere about  $-268^\circ \text{C}$ ., or  $5^\circ$  above absolute zero, it is not surprising that difficulty was experienced. A reference to the methods available for liquefying gases will be found later (pages 265 and 289).

**Gases and Vapours.** It has already been mentioned that sulphur dioxide at a temperature of  $0^\circ \text{C}$ . will liquefy under a pressure of about 1.5 atmospheres. If however the temperature be lowered to  $-10.1^\circ \text{C}$ ., the gas will liquefy under ordinary atmospheric pressure.

Now if we have some water vapour enclosed in a tube and kept at atmospheric pressure it will remain vapour as long as the temperature is above  $100^\circ \text{C}$ ., but if the temperature falls below  $100^\circ \text{C}$ . the vapour will condense, since the vapour pressure of water below  $100^\circ \text{C}$ . is less than 760 mm. of mercury. The two cases are precisely similar; below  $-10.1^\circ \text{C}$ . the vapour pressure



of sulphur dioxide is less than 760 mm. It is usual to talk of sulphur dioxide as a gas and water vapour as a vapour, but the distinction is very arbitrary and arises merely because we happen to live in a climate where the temperature is above the boiling point of sulphur dioxide and below that of water; it would be more logical to regard sulphur dioxide as an unsaturated vapour rather far removed from its saturation pressure. If we wish to make a strict distinction between a gas and a vapour the critical temperature will serve as a criterion; if the substance is below its critical temperature it can be liquefied, and if it is above it cannot. Thus hydrogen above  $-234.5^{\circ}\text{C}$ . may strictly be called a gas; below that temperature it would be an unsaturated vapour at atmospheric pressure until the temperature fell below  $-252.7^{\circ}\text{C}$ . the boiling point of hydrogen.

Water above  $100^{\circ}\text{C}$ . and under atmospheric pressure is an unsaturated vapour, but if the temperature is above  $365^{\circ}\text{C}$ . it passes its critical point and becomes a gas which cannot be liquefied.

**Further Note on the Critical Temperature.**—Turning again to the diagram (Fig. 112) of Andrew's curves for carbon dioxide, there is one point in the interpretation of them which has not yet been considered. In the lowest isothermal, the volume occupied by the substance at B when it is all gas and is just about to liquefy is very much greater than at C, where it has all just become liquid. Thus the density of the gas is much less than that of the liquid. On the next isothermal the corresponding volume change is less. the difference between the density of gas and liquid is less. This difference would diminish for each succeeding isothermal, and just below the critical temperature the difference would be almost nothing, the density of gas and liquid being almost the same. This general effect, which is not confined to carbon dioxide but is characteristic of all substances at this stage, might be well illustrated by an experiment of the following type.

Let Fig. 113 represent a thick-walled glass tube containing some liquid.<sup>1</sup> Let the space above be free from air and contain nothing but the vapour of the liquid (this could be arranged by starting with the tube open at the top, boiling the liquid for some time to drive out air, and then sealing off). The pressure of the

<sup>1</sup> It is desirable not to use water since it attacks glass at high temperatures.



vapour will correspond to the saturation pressure at the particular temperature. Now let the temperature be raised. The saturation pressure being greater, some evaporation will take place and the density of the vapour will increase. At the same time the liquid will expand owing to the increase in temperature, and so will become less dense. Thus as the temperature rises the density of the vapour increases, and that of the liquid decreases. This will go on until, when the temperature is just below the critical temperature, the density of the vapour will be very nearly equal to that of the liquid. The boundary between the two will become less distinct,<sup>1</sup> and finally as the temperature passes the critical point the densities become equal, the boundary disappears and the tube is full of one homogeneous substance; the distinction between liquid and vapour has vanished. Thus the



FIG. 113.

critical temperature may be regarded as the limiting temperature when owing to the density of the liquid and its saturated vapour becoming the same the distinction between them vanishes.

This way of arriving at the idea of the critical temperature was in fact the historical way in which the conception came. The classical experiments were performed by Cagniard de la Tour.<sup>2</sup> His method was similar to that of the preceding paragraph except that he was able to measure the pressure at the same time. The liquid and vapour were contained in the end A (Fig. 114) of the bent tube which contained mercury; the space B contained air, which by its compression indicated the pressure. These experiments were performed many years before those of Andrews; shortly afterwards Faraday succeeded in liquefying a number of gases and considerably extended the knowledge of the effect of pressure and low temperature on a gas.



FIG. 114.

The idea that the distinction between gas and liquid may

<sup>1</sup> The surface tension of a liquid diminishes as the temperature rises, so that the meniscus will become flatter; at the critical temperature the surface tension becomes zero.

<sup>2</sup> *Annales de Chimie et de Physique*, 1822-23.

disappear is further strengthened when we consider that it is possible to pass from an undoubted liquid to an undoubted gas or vice versâ without it being possible to say that the change has occurred at any particular stage. For suppose we have a vessel as in Fig. 115, with the space A filled with a liquid, while B contains air under very great pressure. Let the liquid A be heated until its temperature is above the critical point; if the pressure is great enough, no change takes place except a slight expansion. Now let the pressure in B be released. The substance in A will simply expand like any other gas; there will be no change from liquid to vapour. Thus the substance started as a liquid and finished as a highly compressed gas and at no time was there any abrupt change.

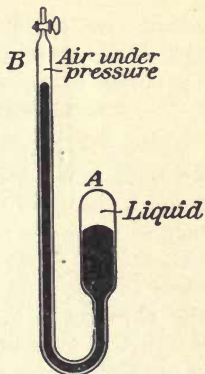


FIG. 115.

**Liquefaction of Gases.**—It is clear that if a gas is at a temperature lower than its critical temperature it can be liquefied by exposing it to sufficient pressure. Gases like sulphur dioxide, chlorine, ammonia, and carbon dioxide, if cooled by means of freezing mixtures, can be liquefied without requiring extravagantly large pressures. (Sulphur dioxide liquefies at atmospheric pressure when cooled below  $-10^{\circ}$  C.) Such gases when liquefied can be used to obtain much lower temperatures by allowing the liquid so formed to evaporate rapidly under reduced pressures and produce cooling by evaporation. This can then be used as the starting-point in the liquefaction of other gases, and was in fact so used in the early experiments on the liquefaction of oxygen. But other methods are necessary in the case of hydrogen, and even for oxygen are far more effective. We shall consider these modern methods in Chapter XIX.

## CHAPTER XVIII

### THE KINETIC THEORY OF GASES

Having considered a few of the outstanding properties of gases, we must now turn to the attempts which have been made to frame a theory of the matter. The object of such a theory is to help us to form a mental picture of what is going on so as to co-ordinate the various observed effects and to anticipate what is likely to happen in any given conditions. From very early times the phenomena of compressibility of matter in all its states, solution of substances in liquids, diffusibility of fluids and the expansibility of gases have led to the idea of matter being constituted of particles with more or less space between them. Various chemical phenomena led to the idea of these particles as molecules each made up of a system of one or more atoms of the same or different natures according to whether the substance is an element or compound, and recent physical work has shown that the atoms themselves are complex systems and atoms of different elements have certain constituents in common. For our present purpose we shall not need to consider anything beyond the molecule, although in one point (see page 305) we shall have occasion to refer to the number of atoms in the molecule.

The characteristic property of a solid is its ability to retain its shape apparently for an indefinite period. This suggests that the molecules are not able to move about from one part of the substance to another. Moreover solids possess cohesion—a great deal of work is necessary to tear one portion of a solid away from another. This suggests that the molecules exert considerable force upon one another. The phenomena of expansion on heating, thermal conductivity, and some connected with radiation, suggest some movement of the molecules, and we may regard each of them as capable of vibrating about some mean position but not of permanent displacement. In the case of liquids, such phenomena as diffusion suggest that the molecules can move about

freely from one part to another ; on the other hand, a liquid has a definite volume at any particular temperature and may also (when free from dissolved gases) show very considerable cohesion. We must therefore regard the molecules as still under the influence of each other's action

A gas has the property of indefinite expansion and hardly appreciable cohesion (but see page 285 on the porous plug effect). We may therefore regard the molecules as moving about freely and for the most part not under the influence of each other's action. The enormous extent to which the volume can be reduced by pressure suggests that the molecules only occupy a very small fraction of the whole volume of the gas. This is the starting-point of the kinetic theory.

On this theory an ideal gas is regarded as made up of a very large number of particles (molecules) of negligible size compared to the volume of the gas, moving about in all directions with considerable velocity and constantly bombarding the walls of the enclosure and colliding with one another. At these collisions no loss of energy occurs, a molecule rebounding from the walls with a velocity equal to that with which it encountered them. The pressure exerted by the gas is regarded as due to this bombardment. Any mutual attractions between the particles are also supposed to be negligible.

Consider a cubical enclosure of side  $s$  (Fig. 116) containing a gas. Let there be  $N$  molecules each of mass  $m$ .

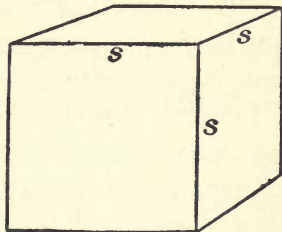


FIG. 116.

Suppose that any particular molecule has a velocity  $u$  in any direction. We can resolve this velocity into three components  $x$ ,  $y$ ,  $z$ , parallel to three adjacent edges of the cube. Since these directions are mutually at right angles, we have by the ordinary resolution of vectors,

$$x^2 + y^2 + z^2 = u^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We can deal with each of these components separately. Considering the pair of faces of the cube perpendicular to the  $x$  axis, a molecule starting at one face will travel to the other, bound back and arrive back at the face from which it started in the

time it takes to travel  $2s$  with velocity  $x$ , i.e. in  $\frac{2s}{x}$  seconds. It will therefore collide with this face  $\frac{x}{2s}$  times per second.<sup>1</sup>

At each collision its momentum is changed from  $mx$  in one direction to  $mx$  in the opposite, i.e. the change of momentum is  $2mx$ . Since this occurs  $\frac{x}{2s}$  times per second, the rate of change of momentum is  $\frac{x}{2s} \times 2mx = \frac{mx^2}{s}$ . But the rate of change of momentum is equal to the force exerted on the face. Thus on each pair of faces perpendicular to the  $x$  axis there is a force exerted due to this molecule of  $\frac{mx^2}{s}$ .

In the same way on each of the faces perpendicular to the  $y$  axis there is a force  $\frac{my^2}{s}$ , and on each of the other pair the force is  $\frac{mz^2}{s}$ .

The total force exerted on all the faces is thus

$$\frac{2mx^2}{s} + \frac{2my^2}{s} + \frac{2mz^2}{s} = \frac{2m(x^2 + y^2 + z^2)}{s} = \frac{2m\bar{u}^2}{s} \text{ by (1).}$$

The force will not, of course, be the same on each face (unless it so happened that  $x = y = z$ ).

If another molecule had a velocity  $u_1$ , the total force on all faces exerted by it would in the same way be  $\frac{2m\bar{u}_1^2}{s}$ . Thus the total force exerted by the  $N$  molecules would be

$$\frac{2m}{s} (\bar{u}^2 + \bar{u}_1^2 + \bar{u}_2^2 + \dots)$$

where  $\bar{u}$ ,  $\bar{u}_1$ ,  $\bar{u}_2$ , etc., are the respective velocities of the  $N$  molecules.

Let  $\bar{U}^2$  be the mean value of  $\bar{u}^2 + \bar{u}_1^2 + \dots$

<sup>1</sup> The argument is not affected by the fact that it may collide with another molecule on the way. Suppose the second molecule happened to be at rest when the collision occurred. It would move off with velocity  $x$  and the first would come to rest. Thus a molecule would still go on with velocity  $x$  even though it were not the same one. The resultant effect is the same whatever the velocities provided no energy is lost in collision.





$\bar{U}$  remains constant. Thus for any given mass of gas at constant temperature

$$pv = \text{constant.}$$

**Charles's Law.**—If we consider that the addition of equal amounts of energy produces equal rise of temperature (i.e. the Thermal Capacity of the gas remains constant at all temperatures), then the internal energy of a given mass of gas will be proportional to its absolute temperature. Thus  $\frac{1}{2}Nm\bar{U}^2 \propto T$ , but  $pv = \frac{1}{3}Nm\bar{U}^2$ .

$$pv \propto T \text{ or } pv = RT \text{ where } R \text{ is a constant.}$$

**Graham's Law of Diffusion.**—Since

$$\begin{aligned} pv &= \frac{1}{3}Nm\bar{U}^2 \\ &= \frac{1}{3}M\bar{U}^2 \text{ where } M \text{ is the total mass of gas,} \\ p &= \frac{1}{3} \frac{M}{v} \cdot \bar{U}^2. \end{aligned}$$

But  $\frac{M}{v}$  is the mass per unit volume or the density.

If  $\rho$  is the density we have therefore

$$p = \frac{1}{3} \rho \bar{U}^2.$$

This means that at any particular pressure the value of  $\rho \bar{U}^2$  is the same for all gases, or that

$$\bar{U}^2 \text{ is proportional to } \frac{1}{\rho}.$$

Graham found that the rates of diffusion of gases were inversely proportional to the square roots of the densities.

**Avogadro's Hypothesis.**—Suppose we have two gases, each at the same pressure  $p$ , and let  $n_1$  be the number of molecules per unit volume,

$m_1$  be the mass of each molecule,

$\bar{U}_1$  be the root mean square of the velocity

for the one gas, and  $n_2, m_2, \bar{U}_2$  the values for the other gas.

$$\text{Then } p = \frac{1}{3} n_1 m_1 \bar{U}_1^2.$$

$$\text{But } p = \frac{1}{3} n_2 m_2 \bar{U}_2^2.$$

$$\text{Thus } n_1 m_1 \bar{U}_1^2 = n_2 m_2 \bar{U}_2^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now if the two gases be allowed to mix, and have no chemical action on each other, there will be no evolution or absorption of heat. This means there is on the whole no communication of energy from one gas to the other; each set of molecules remains as before.

But it is a proposition in statistical mechanics, known as Maxwell's Law of equipartition of energy, that when a system in equilibrium is made up of a number of components, each component being able to possess one kind of energy, the total energy of the system will on the average be equally divided amongst the components. In this case the components are the  $n_1$  molecules of one kind and the  $n_2$  molecules of the other, each of which can possess kinetic energy of translation. Thus on the average a molecule of one kind will have the same energy as that of another, thus  $\frac{1}{2} n_1 \bar{U}_1^2 = \frac{1}{2} n_2 \bar{U}_2^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$

It follows from (3) and (4) that

$$n_1 = n_2.^1$$

**Influence of the Action of one Molecule on another.**—The kinetic theory which has just been outlined deals with the case of an ideal gas in which the influence of one molecule on another is negligible. The phenomenon of cohesion (to say nothing of any others) indicates that when the molecules are fairly closely packed they do have a decided action on each other, and so it is not surprising that actual gases show some deviation from Boyle's Law and other simple relations, especially when they are highly compressed.

We will now consider how the simple kinetic theory can be modified so as to take account of this effect and be brought more into accordance with observed results. The first really satisfactory modification is due to Van der Waals in 1879.

There are two aspects of this effect to be considered. First

<sup>1</sup> It should be noticed that this demonstration of Avogadro's Hypothesis is based on a piece of statistical mechanics (Maxwell's Law) which involves conceptions far beyond the scope of this book. It is a fundamental proposition of the classical Newtonian mechanics, but experience is necessary to decide when the conditions are such as to make it safe to apply it.

the actual size of the molecules diminishes the space available for movement, and collisions with the bounding walls are therefore made more frequent. Thus if we imagine a molecule A (Fig. 117) travelling from one wall of the vessel to the opposite, it is clear that the distance it has to go is not the width of the vessel, but

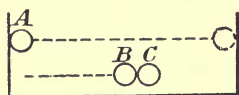


FIG. 117.

that width minus the diameter of the molecule. In the same way if the molecule B collides with a molecule C which is at rest, C moves off with a corresponding velocity and hits the opposite wall, so that the effect is the same as if B had gone on; only C

starts off not from the point where B stops but one diameter to the right of it. This general effect may be summed up by saying that the volume available for movement is not the observed volume  $v$  of the gas but  $v - b$  where  $b$  is a space proportional to the volume occupied by the molecules themselves.<sup>1</sup>

Secondly, the force exerted by one molecule on another. Cohesion suggests that there is an attraction between them which is considerable when the molecules are close together; but the behaviour of gases suggests that the force becomes small when the distance is large. In the present state of our knowledge we cannot say very much about the nature of this force, but for the moment we may consider that when two molecules are within a certain distance of each other there is a force of attraction between them, but beyond this distance the force is negligible. We may express this by saying that each molecule has a sphere of influence of a certain radius; any molecule which comes within this sphere will suffer attraction.

The general effect of this is that in addition to the external pressure tending to prevent the molecules passing out in all directions there is a mutual attraction between the molecules.

At any given moment this attraction will only be operating on any molecules which happen to be within the sphere of influence of another; the total effect will therefore be proportional to the

<sup>1</sup> It might be thought at first sight, that  $b$  is equal to the volume of the molecules; detailed consideration shows that this is not so. Van der Waals concluded that  $b$  was four times this volume, and Jeans has arrived at the same conclusion. An elementary treatment (which, however, requires following with care) is given in Poynting and Thomson's *Heat*, page 153.

frequency with which such close approaches happen. Now on the ordinary laws of probability the chance of one particular molecule coming within a certain distance of some other molecule is proportional to the number of such molecules per unit volume; the chance of any molecule coming within this distance of any other is therefore proportional to the square of this number.

The frequency of such approaches will therefore be proportional to  $\frac{1}{v^2}$ , and so to get the total restraining influence we must

add to the pressure a term proportional to  $\frac{1}{v^2}$ .

Instead of putting the simple relation

$$pv = RT$$

Van der Waals puts

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \text{ where } a \text{ is a constant.}$$

It should be noticed that as far as deviations from Boyle's Law are concerned the two effects operate in contrary directions.

For if, instead of  $pv = \text{constant}$

$$\text{we put } p(v - b) = \text{constant,}$$

$$\text{we have } pv = pb + \text{constant,}$$

in other words,  $pv$  increases with pressure.

On the other hand, if instead of  $pv = \text{constant}$

$$\text{we put } \left(p + \frac{a}{v^2}\right)v = \text{constant,}$$

$$\text{we have } pv = \text{constant} - \frac{a}{v}$$

and therefore  $pv$  diminishes as  $v$  diminishes or  $p$  increases. What actually happens will depend on which factor is of more importance.

In the case of hydrogen where  $pv$  increases with pressure, it appears that the attraction between the molecules is of small effect

<sup>1</sup> This was not the way in which Van der Waals arrived at the term  $\frac{a}{v^2}$  in his expression, but it appears to the writer to have some advantages,

and in particular to make it clearer why the same term  $\frac{a}{v^2}$  is not to be expected to express the relation when the compression is so great that the molecules are practically always within each other's sphere of influence.



compared with the other factor. (Cp. page 289.) In gases like air and nitrogen, however, the effect of the attraction is at first predominant and  $pv$  diminishes; when the compression becomes sufficiently great the size of the molecules as compared to the total volume becomes the predominant factor.

Van der Waals' equation is a much closer representation of the observed facts in connection with gases than the simple equation  $pv = RT$ . In the case of some substances (halogen derivatives of benzene) it is obeyed fairly closely both in the gaseous and liquid states. In the case of other substances, however, it does

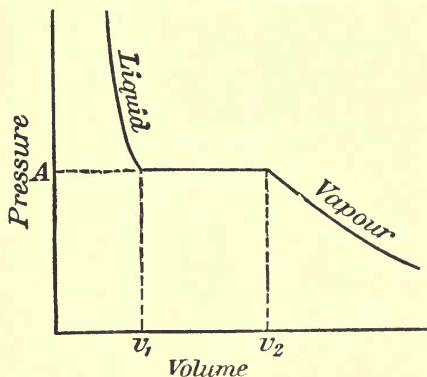


FIG. 118.

not very well represent the facts for both states. This is not very surprising, since in the liquid state the molecules are probably within the sphere of one another's influence, and in that case, as pointed out in the footnote, page 273, one would not expect a simple constant  $a$  to represent the facts. Until we know more about the nature of molecular forces it is

not likely that a satisfactory formula can be found. In the meantime Van der Waals' equation represents a very valuable help in visualizing what is happening and is undoubtedly on the right lines.

There is one aspect of Van der Waals' equation which is of considerable importance.

If we take the equation

$$\left(p + \frac{a}{v^2}\right) (v - b) = RT$$

it will be seen that it is a cubic equation for  $v$ . For it may be written

$$\begin{aligned} (pv^2 + a)(v - b) &= RTv^2 \\ \text{or } pv^3 - (bp + RT)v^2 + av - ab &= 0, \\ \text{i.e. } v^3 - \left(b + \frac{RT}{p}\right)v^2 + \frac{av}{p} - \frac{ab}{p} &= 0. \end{aligned}$$

Now a cubic equation has three roots, of which either one or three are real.

This means that for any given value of  $p$  and  $T$  there are either one or three possible values of  $v$ .

Taking the case of an isothermal for a substance below its critical point (Fig. 118).

For any value of  $p$  above the point A there is only one possible value of  $v$ , and similarly for a point below A. But for the value A the volume can be  $v_1$  (all liquid) or  $v_2$  (all vapour), or we could have a mixture of the two at some intermediate value.

Now from quite different considerations, based partly on the fact that it is possible to cool a vapour some way below its condensing point (in the absence of dust or any suitable condensation nuclei) and also to heat a liquid above its boiling point, James Thomson suggested that ideal form of the isothermal might be a continuous curve of the form shown (Fig. 119), where the

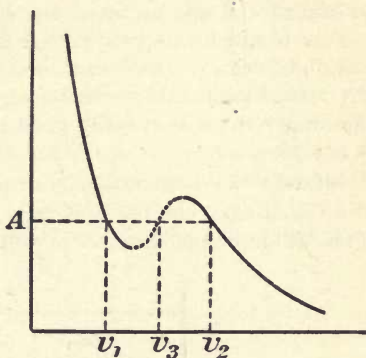


FIG. 119.

dotted part represented an unstable state. In this case the third root of our equation would be represented by  $v_3$ . This is purely hypothesis. What is of real meaning is that at the critical temperature, the points  $v_1, v_2, v_3$  coincide. But in this case the value of  $p$  and  $T$  must be such that the equation is of the form of a perfect cube. If  $p_c$  and  $T_c$  are the values of the critical pressure and temperature, then

$$v^3 - \left(b + \frac{RT_c}{p_c}\right)v^2 + \frac{a}{p_c}v - \frac{ab}{p_c} = 0$$

must satisfy the condition

$$(v - v_c)^3 = 0.$$

Equating coefficients we have

$$b + \frac{RT_c}{p_c} = 3v_c$$

$$\frac{a}{p_c} = 3v_c^3$$

$$\frac{ab}{p_c} = v_c^3$$

Thus

$$b = \frac{v_c}{3}$$

$$a = 3p_c v_c^3$$

$$RT_c = \frac{8a}{27b}$$

Thus there is a definite relation between the critical data of any substance and the value of the constants  $a$  and  $b$ .

Now  $a$  and  $b$  can be deduced from observations of the compressibility of a gas such as those of Amagat. Using these values the critical temperature can be calculated.<sup>1</sup> The agreement with the observed value is fairly good in some cases, but in others it is not so good.

**Note on Evaporation.**—It is interesting to consider the behaviour of a liquid from the point of view of the kinetic theory. Let A (Fig. 120) represent a molecule well within the liquid. It is acted

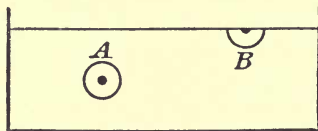


FIG. 120.

upon only by those molecules within its sphere of influence, so that if it is in the position A it will suffer attractions in all directions. These on the average will balance and so there will be no resultant force tending to prevent it moving. But if it gets to the surface as at B the available attractions will be downwards, and to get out from the surface it will have to overcome this attraction. Thus the molecules in the surface layer will be under the constraint of forces which tend to keep them in the liquid. This constraint manifests itself in the phenomenon known as surface tension.

Now the molecules in the liquid are moving about, and if one

<sup>1</sup> Cp. the work of Kammerlingh Onnes in calculating the conditions necessary to effect the liquefaction of helium, p. 292.

comes to the surface it may be going fast enough to get out ; if it is not it will be retained. The escape of the molecules represents evaporation, and it will be obvious that the higher the temperature of the liquid the greater will be the number of fast moving molecules and therefore the greater the rate of evaporation.<sup>1</sup>

If the space above the liquid is enclosed the molecules forming the vapour will be moving about in this space, and some of them may strike the surface of the liquid and so pass into it again. The number of those which do so will be greater the greater the amount of vapour in the space. Finally a state of equilibrium will be reached when the number of molecules escaping from the liquid per second is equal to the number which re-enter it. This is the condition when the space is said to be saturated.

It is clear that since the rate of evaporation increases with temperature the pressure of the vapour in the space will have to be greater at high temperatures in order that the number of molecules entering the liquid may balance those which get out. Hence the saturation pressure of a liquid will increase with temperature.

<sup>1</sup> There is a definite connection between the latent heat of evaporation of a liquid and its surface tension. Cp. Hammick, *Phil. Mag.*, August, 1919, "Latent Heat and Surface Energy."

## CHAPTER XIX

### PROPERTIES OF A GAS—ENERGY CONSIDERATIONS—LIQUEFACTION OF GASES

**Work done by a Gas Expanding.**—If we have a quantity of gas under a given pressure and the gas is made to expand, e.g. by heating it, work is done against the external pressure. To illustrate this point let us suppose that we have some gas in a

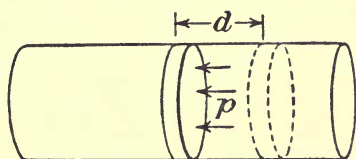


FIG. 121.

cylinder fitted with a piston which works without friction (Fig. 121), and is exposed to the external pressure  $p$ . Let the area of the piston be  $A$ ; then the external force acting on it is  $pA$ . Now let the gas expand and push the piston

out through a distance  $d$ ; the work done against the external force is  $pA \times d$  or  $pAd$ . But  $Ad$  is the increase in volume of the gas and so the work done is  $p(v_2 - v_1)$ , where  $v_2$  is the final volume and  $v_1$  the initial volume. We have imagined the presence of a piston in order to fix our mind on the enclosed gas and see what it is doing, but it is clear that the gas has to do this work against the external pressure whether the piston is there or not, since it has to make the extra room  $v_2 - v_1$  for itself against the external pressure.<sup>1</sup>

In many practical cases the pressure does not remain constant

<sup>1</sup> It should be noticed that the shape of the enclosure occupied by the gas does not affect the work done; for if the volume has reached the value  $v_2$  in any way no work is done in altering the shape at constant volume since any force, however small, will alter the shape of a fluid. We can see this is so by imagining a number of side tubes fitted with pistons. If we push one in the others must move out in such a way that the increase in volume due to the pistons moving out is equal to the decrease due to those moving in, and the work done in the two cases is  $p \times v$  and  $-pv$  respectively.



as the gas expands. If, however, we know how the pressure varies we can still find the work done. Let us suppose that the pressure and volume of a gas are represented by the curve AB, Fig. 122; for example, the gas may be kept at constant temperature, in which case AB is the ordinary isothermal curve. Consider the work done as the volume increases by a series of small stages. Let the first stage be from  $v_1$  to X represented by the points A and C on the curve. If the pressure at A is  $p_1$  and the pressure at C is  $p_x$ , we shall only make a small error if we take the work

done as  $(X - v_1) \times$  average pressure or  $\frac{p_1 + p_x}{2} \cdot (X - v_1)$ . This

is represented on the diagram as the area of the rectangle HKX $v_1$ .

Similarly the work done from X to Y will be represented by the area LMYX.

The work done from  $v_1$  to  $v_2$  will therefore be the sum of all the rectangles shown by the dotted lines; that is to say, it is the area of the figure  $v_1$ HKLM...TU $v_2$ .

If the different stages are taken much smaller, the zigzag line HKLM...U will become nearer to the curve AB, and

if the steps are made indefinitely small the zigzag line will, in the limit, coincide with AB. Thus the work done is actually represented by the area AB $v_2v_1$ , that is to say by the area bounded by AB, the two ordinates at  $v_1$  and  $v_2$  and the axis of volumes. This process is only a graphical representation of the process of integration, so that in the notation of the calculus we can say

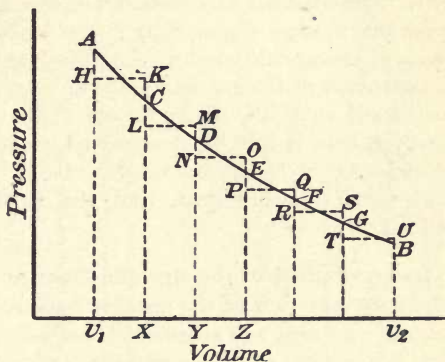


FIG. 122.

$$\text{Work done against external pressure} = \int_{v_1}^{v_2} p dv.$$

Thus so long as we know the form of the curve representing the relation of pressure and volume we can calculate the external work done.

When the gas expands, the energy to do this external work has to be supplied from somewhere ; if it is not supplied, and some compressed gas is allowed to expand against external pressure, the energy to do the external work is taken from the gas itself, which becomes cooler. For example, the thermal capacity of a given mass of gas will be greater if we keep the pressure constant and let the gas expand as its temperature rises than it will be if we keep the volume constant ; in the one case external work is done and in the other it is not. In speaking of the specific heat of a gas it is therefore necessary to state the conditions ; we speak of the specific heat at constant pressure and the specific heat at constant volume respectively ; the ratio of these two specific heats is usually denoted by  $\gamma$ . The value of  $\gamma$  depends on the constitution of the gas and plays an important part in problems connected with the energy ; we shall see, in the succeeding chapter, that it can be determined without finding the values of the specific heats separately. It is, however, possible to find either specific heat, and the methods available are as follows.

#### Determination of the Specific Heat at Constant Pressure.—

The determination of the specific heat at constant pressure of a number of gases was successfully carried out many years before the difficulties of the constant volume determination were overcome.

Regnault <sup>1</sup> carried out a number of experiments, and his method may be indicated as follows :—

The general idea was to pass the gas through a heating coil, whereby its temperature was raised to some particular value, and then to let it flow through a thin metal vessel contained in a calorimeter and so measure the heat given up. The pure dry gas was contained in a large reservoir A (Fig. 123), which was provided with an open manometer B. A was kept at a constant temperature by a water bath, and the amount of gas which had passed out was determined from the reading of the manometer before and after the experiment. The volume of the reservoir

<sup>1</sup> *Mémoires d'Académie des Sciences*, vol. 26, 1862.

being known and the temperature constant, the quantity of gas was calculated from the fall in pressure.<sup>1</sup>

The gas passed through a regulating valve C; beyond this valve was a water manometer G, and C was gradually opened as the experiment proceeded, so that the pressure indicated by G remains constant. Thus although the pressure in the reservoir was falling the rate of flow of gas remained steady, and the pressure at which it entered the calorimeter was constant.

The gas passed through a spiral tube of thin copper, immersed in a vessel of oil D, heated by a spirit lamp. This tube was so long (about 10 metres of tubing) that by the time the gas reached its lower end it had taken up the temperature of the oil bath.<sup>2</sup>

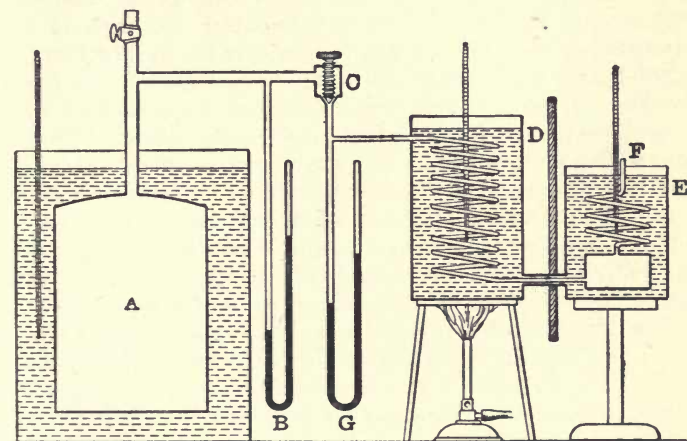


FIG. 123.

The gas then entered the calorimeter E; here it passed through a vessel made of thin brass shown diagrammatically in the sketch; actually it consisted of a number of chambers with partitions, so that the gas flowed against a large surface of the walls

<sup>1</sup> To make sure of the accuracy of this method, a subsidiary experiment was performed in which the escaping gas was collected and weighed and the weight compared with that calculated from the manometer readings.

<sup>2</sup> Subsidiary experiments were made with a thermometer in the tube to make sure that the gas did take up this temperature.

of the vessel. Finally it escaped to the atmosphere at F. A thermometer at F showed that the temperature of the escaping gas was the same as that of the calorimeter. If  $T$  is the temperature of the gas entering the calorimeter and  $t_1$  and  $t_2$  the initial and final temperatures of the calorimeter and contents, the average fall in temperature of the gas is  $T - \frac{t_1 + t_2}{2}$ , and hence the heat given up by the gas is  $ms\left(T - \frac{t_1 + t_2}{2}\right)$ .

In order to prevent, as much as possible, transference of heat from the heater to the calorimeter by conduction along the tube the connecting part was made of non-conducting material. The heater and lamp were surrounded by an outer vessel to diminish radiation to the calorimeter, and the latter was enclosed in a wooden box, one side of which is represented at D (Fig. 123). In making the experiment, observations were first made for an interval of ten minutes, without having any gas flowing, to determine the rate at which the calorimeter received heat by conduction and radiation; the gas was then turned on and the rise in temperature of the calorimeter and its contents noticed; finally the gas was stopped and the rate of change of temperature of the calorimeter noted; in this case we have the cooling effect of the calorimeter to the surroundings superposed on the heating effect due to conduction and radiation from the heater.

The difficulty of this experiment lies in the fact that the gas must pass through fairly slowly in order to be sure that it finally attains the temperature of the calorimeter; but this means that the passage of gas must go on for some time if sufficient mass is to pass through to give a reasonable rise in temperature. The various corrections therefore represent an important fraction of the whole effect, and it is in the evaluation of these corrections that the trouble comes in. It is a tribute to the skill of Regnault that his results agree as well as they do with those obtained by later and improved methods.<sup>1</sup>

**Specific Heat at Constant Volume.**—In this case the gas must be enclosed in some vessel, and the mass of this vessel will be large compared to that of the gas. The relatively large thermal

<sup>1</sup> A fairly full account of later work, especially that of Lussana, is given in Preston's *Theory of Heat*, 3rd edition. Mention should also be made of the work of Swan (*Proc. Roy. Soc.*, Dec., 1908) and others.

capacity of the container presented great difficulties, and it was not until the introduction of the steam calorimeter by Joly that satisfactory direct determinations were made.<sup>1</sup> For this purpose Joly<sup>2</sup> used a modified form of his apparatus which he called a differential steam calorimeter.

Two equal copper spheres (Fig. 124), 6.7 cm. in diameter, hung from opposite arms of the balance in the same steam chamber. Catchwaters A A were fitted to catch any of the condensed steam which might drop off the spheres. The two spheres with their catchwaters were made of equal thermal capacity. One sphere was empty and the other contained the gas under experiment at a considerable pressure—in some cases 20 atmospheres or more. The excess of condensation on the one side over that on the other gave the condensation due to the contained gas; the effect of the thermal capacity of the containers and their buoyancy effect (see page 169) were thus eliminated.

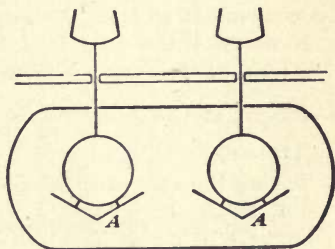


FIG. 124.

The great merit of this arrangement is that the quantity of heat absorbed by the gas as its temperature is raised is directly determined; it does not appear as the difference between two large quantities separately determined.

SPECIFIC HEATS OF GASES BY DIRECT DETERMINATION.

	Constant pressure.	Constant volume.
Hydrogen . . . . .	3.40	2.40
Nitrogen . . . . .	.23	.17
Air . . . . .	.24	.17
Carbon dioxide . . . . .	.20	.16
Argon . . . . .	.12	.075

<sup>1</sup> Up to this time the value of the specific heat at constant volume was calculated from that at constant pressure by the methods indicated on page 298.

<sup>2</sup> *Phil. Trans.*, 1891.



**Mayer's Calculation of the Mechanical Equivalent of Heat from the Values of the Specific Heats of a Gas.**—If the difference between the specific heats of a gas is solely due to the fact that when the gas expands it does work against the external pressure, we can obtain a value for the mechanical equivalent of heat since the coefficient of expansion of the gas is known. This was suggested by Mayer <sup>1</sup> in 1842; he took the case of air and worked out a value for J. At that time, however, the available data in connection with specific heats of gases were very unreliable, and the value he obtained is of little interest. We may illustrate the method by taking modern results; it will be convenient to take the case of hydrogen.

If we take the weight of 1 litre of hydrogen at 0° C. and 760 mm. of mercury as 0.0899 gms. the volume of 1 gm. of hydrogen at this temperature and pressure is  $\frac{1}{.0899}$  litres or 11,130 c.c.

Taking the value for the coefficient of expansion of hydrogen as  $\frac{1}{273}$  (cp. page 75), the increase in volume of 11,130 c.c. when heated from 0° C. to 1° C. is  $\frac{11,130}{273}$  c.c. The pressure is 76 cm. of mercury or  $76 \times 13.6 \times 981$  dynes per sq. cm.

The work done is therefore  $p \times (v_2 - v_1)$

$$= \frac{76 \times 13.6 \times 981 \times 11,130}{273} \text{ ergs.}$$

This work accounts for the difference between the thermal capacity of 1 gm. of hydrogen at constant pressure and constant volume respectively. This difference is  $3.40 - 2.40 = 1$  calorie.

Thus 1 calorie is equivalent to

$$\frac{76 \times 13.6 \times 981 \times 11,130}{273} \text{ ergs} = 4.13 \times 10^7 \text{ ergs.}$$

**Internal Work when a Gas Expands.**—The method of calculating J which has just been given depends on the assumption that when a gas expands the only work it has to do is in pushing back the external pressure. If, however, there is a mutual attraction between the molecules work will also be done in pulling them further apart; this may be spoken of as the internal work. Mayer assumed that no internal work was needed; Joule, who

<sup>1</sup> *Liebig's Annalen*, 1842.

began his work on the mechanical equivalent of heat in 1840, made a number of experiments in connection with this point. Two copper reservoirs A and B (Fig. 125) were connected by a pipe fitted with a tap. A contained dry air at a pressure of 22 atmospheres, and B was exhausted. The two reservoirs were placed in a calorimeter. On opening the tap air rushed from A to B until the pressure was the same in each; no external work was done since the gas does not have to push back the atmospheric pressure. On the other hand, if there is a mutual attraction between the molecules work will have to be done in increasing the distance between them, and the gas will tend to absorb heat from its surroundings to supply the necessary energy. Joule was not able to detect any fall in temperature of the water in the calorimeter although his thermometers read to  $\frac{1}{10}^{\circ}$  F., and the calorimeter was shaped so that the quantity of water required to cover the reservoirs was as small as possible. The experiment was tried with A and B in separate calorimeters, in which case there was a distinct cooling effect in A's calorimeter and a nearly equal heating effect in B's. These experiments indicated that the internal work was inappreciable and appeared to justify Mayer's assumption. But the thermal capacity of the reservoirs and the calorimeter were so large in comparison with that of the gas that unless the cooling effect was considerable it was likely to escape detection. All that the experiments showed was that there was no large effect.

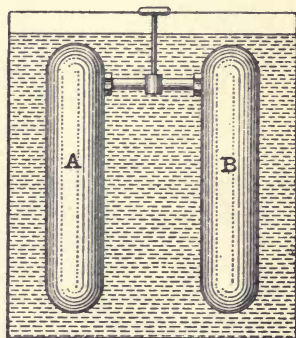


FIG. 125.

A more sensitive method was proposed by Sir W. Thomson (Lord Kelvin), and he and Joule carried out a series of experiments in 1852 which gave decisive evidence of internal work. These experiments are of fundamental importance (see pages 319 and 290) and must now be considered.

**The Joule-Thomson Porous Plug Experiments.**<sup>1</sup>—The general

<sup>1</sup> Thomson, *Math. and Phy. Papers*, vol. 1. Joule, *Scientific Papers*, vol. 2. *Phil. Trans.*, 1853 and 1854, 1862.

idea in these experiments is to cause the gas under pressure to flow along a tube in which there is a very constricted opening at one point which results in a considerable drop in pressure; such an arrangement would be referred to by engineers as throttling.

Let Fig. 126 represent a pump driving gas along the tube in which there is a narrow constriction. Eddies are formed by the gas rushing through the constriction, but these subside a little beyond the opening as their energy is frittered away. Let

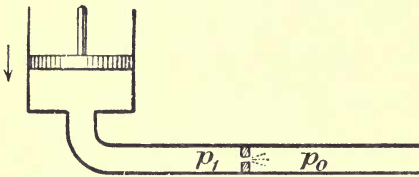


FIG. 126.

us suppose that the tube is of large diameter so that the velocity of the gas is very small except near the opening and its kinetic energy negligible, and let a steady state have been reached. Let  $p_1$  be

the pressure in the tube on one side of the opening and  $p_0$  that on the other; if the tube is open to the atmosphere (as it was in the actual experiments)  $p_0$  will be sensibly equal to the atmospheric pressure (since the velocity of the gas is small).

Suppose that in a certain time a mass of gas  $m$  has passed through the opening. Let  $v_1$  be the volume occupied by this gas under a pressure  $p_1$ , and  $v_0$  its volume under pressure  $p_0$ . The passage of this gas into the low pressure side of the tube means an increase in volume  $v_0$  on this side and involves pushing back the atmospheric pressure; the work done is therefore  $p_0 v_0$  (page 278).

But the volume of gas in the high pressure side has diminished and the pump has therefore done an amount of work on the gas equal to  $p_1 v_1$ . If the gas obeys Boyle's Law,  $p_1 v_1 = p_0 v_0$ .

The amount of work done on the gas is therefore equal to that done by it, and the gas does not have to draw on its own energy to do the work of expansion.

Thus as far as external work goes there would be no reason for any change in temperature of the gas.

But if work is necessary to separate the molecules against their mutual attraction some energy must be supplied to do the necessary work in expanding from  $v_1$  to  $v_0$ . This additional energy would have to be supplied by the gas itself, and so the tempera-

ture would fall. It was this effect that Joule and Thomson looked for.

One modification of the arrangement of Fig. 126 was necessary. The gas issuing from the hole has a large velocity and therefore kinetic energy. If the total energy of the gas is not altered it must have less energy of other kinds and its temperature would therefore be lower.<sup>1</sup>

Further on where the eddies have subsided this kinetic energy has been reconverted to heat and the temperature would be restored. It would not do, therefore, to seek for a cooling effect by taking the temperature close to the orifice, while further on the gas has had a chance of receiving heat from the walls of the tube and other sources, and a small effect would be missed. For this reason Joule and Thomson replaced the simple aperture with a porous plug of cotton wool (in some cases silk fibres) confined by two perforated brass plates (Fig. 127). In this way the gas which issued possessed

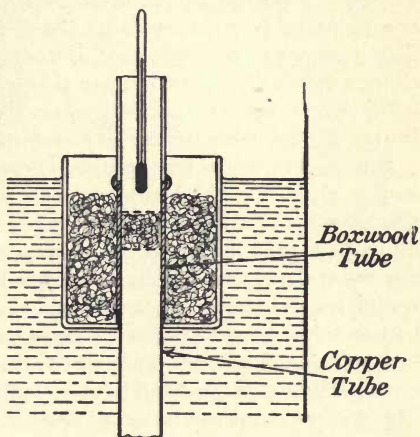


FIG. 127.

hardly any kinetic energy. The gas was passed at a slow steady rate through a long spiral copper tube immersed in a water bath at constant temperature. The upper end of the tube terminated in a short boxwood tube containing the plug. A thermometer was suspended immediately above the plug and a portion of the tube was made of glass to enable the thermometer to be read. Surrounding the boxwood tube was a metal jacket filled with cotton wool, to protect the tube from the influence of external heat, in contact with the boxwood tube. The gas was allowed to pass for a considerable time (about an hour) before

<sup>1</sup> A large effect of this kind was in fact found by Joule and Thomson in a subsidiary experiment with a simple orifice.

taking any readings in order to allow initial fluctuations of temperature to subside and make sure that a steady state had been reached.

They found that in the case of all gases except hydrogen there was a cooling effect, which was much more marked for carbon dioxide than for air, oxygen or nitrogen. Hydrogen, however, gave a slight but distinct heating effect. In all cases the thermal effect was proportional to the difference in pressure on the two sides of the plug.

At first sight the behaviour of hydrogen appears to be very extraordinary, but in the interpretation of these results there is one point to be remembered. In the simple treatment of page 286, it was pointed out that if the gas obeys Boyle's Law no change in the energy of the gas is brought about by the external work done; the work done  $p_1v_1$  on the gas (the energy supplied by the pump) being equal to the work  $p_0v_0$  done by the gas.

But no gas obeys the Law absolutely, and if  $p_1v_1$  is not equal to  $p_0v_0$  there is a balance of external work to be considered. For pressures such as were used in this experiment the value of  $p_v$  for all gases except hydrogen diminishes with pressure, i.e. the gases are more compressible than Boyle's Law indicates. Thus  $p_1v_1$  would be less than  $p_0v_0$ , and so the work done on the gas would be less than the external work done by it; the energy necessary for the balance of work done by the gas would be drawn from the gas itself, and there would be a cooling effect on this account. This cooling effect can be calculated for any gas by using Amagat's values for the variation of  $p_v$ . When this is done it is found that it is very much less than that observed by Joule and Thomson, so that there still remains a decided cooling effect due to internal work.<sup>1</sup>

In the case of hydrogen  $p_v$  increases with pressure, and thus  $p_1v_1$  is greater than  $p_0v_0$ , so that the external work done on the gas is greater than that done by it. There is thus a heating effect due to this cause. When the value is worked out from Amagat's value for the deviation from Boyle's Law it is found to be about the same magnitude as that observed by Joule and Thomson. It follows therefore that in the case of hydrogen at moderate

<sup>1</sup> For example, in the case of air, the cooling due to this deviation from Boyle's Law only amounts to a little over  $\frac{1}{10}$  of the total effect observed.



pressures the mutual action of the molecules upon one another is very small indeed.

**Temperature Inversion of the Cooling Effect.**—Joule and Thomson found that the cooling effect diminished as the initial temperature of the gas was increased. Later work has shown that for every gas there is some temperature at which the cooling effect becomes zero, and that above this temperature a heating effect is observed. Hydrogen, as we have seen, gives a heating effect, but at sufficiently low temperatures it is found to give a cooling effect.

Olszewski found that the temperature of inversion for hydrogen was  $-80.5^{\circ}\text{C}$ .; below this temperature there is a cooling effect and above it a heating. This point is of great importance in the liquefaction of hydrogen.

### Liquefaction of Gases.

The work done by an expanding gas is the basis of the successful methods of liquefying the more permanent gases. In the early work the gas was compressed to a very high pressure in a vessel cooled by suitable refrigerators such as liquid carbon dioxide, and the pressure then suddenly released, e.g. by opening a tap. The gas rushed out, doing work against the external pressure and thereby became cooled; if the initial pressure were high enough some of the gas liquefied. In this way oxygen was first liquefied in 1877 by Cailletet and Pictet, working independently.

The method was developed, and a better refrigerating substance for the initial cooling was rapidly evaporating liquid ethylene. Oxygen, nitrogen and air were thus liquefied, and about 1883 Wroblewski succeeded in liquefying hydrogen, and later Olszewski obtained an appreciable quantity.

**Modern Methods.**—The method described above is not suitable for the production of considerable quantities; some form of continuous process is needed. The introduction of the regenerative method of cooling marked the beginning of a new period in the history of the subject. The method may be indicated by the following outline of a process suitable for a gas such as air.

The air is compressed to a very high pressure by a pump A (Fig. 128) and passes through a coil of copper piping B in a water tank whereby the heat generated in compression is absorbed and the gas passes on, at atmospheric temperature through a long

copper spiral C. At the lower end is a nozzle D, the opening of which is controlled by a valve.

There it expands down to atmospheric pressure and cools. The cooled gas sweeps up past the coil and thereby cools the next portion of gas coming down inside the coil. Successive portions of the oncoming gas are cooled further and further until at last, if the initial pressure is sufficient,<sup>1</sup> some of the gas liquefies and is

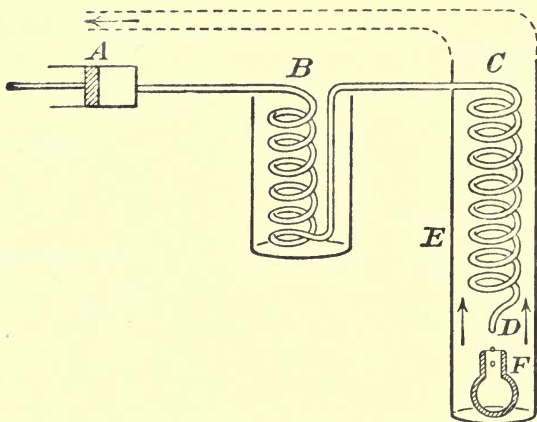


FIG. 128.

collected in a vessel F. The coil is surrounded by a vessel E of good heat insulating material.

The conditions under which the expansion is done are quite different from those of the older method of Pictet and others. The compressed gas is being driven by the pump along the system, and hence although work is being done at the nozzle in expanding against atmospheric pressure, the energy to do it is mainly derived from the gas behind, which in turn is receiving it from the pump. The conditions are therefore almost similar to those of the porous plug experiment, and the cooling effect is chiefly due to the Joule Thomson effect of internal work. This effect, which is almost insignificant at moderate pressures, becomes quite large at high pressures and low temperatures.

<sup>1</sup> A pressure of about 200 atmospheres or a little less is a typical pressure for liquid air apparatus.

This point becomes clearer when we consider the arrangement for gases other than air. It should be noticed that the gas coming down the spiral C is cooled by the expanded gas passing up outside it; the latter is therefore receiving heat, and its temperature rises as it passes up E. There must be a sufficient length of tubing in C to enable a suitable exchange of heat to take place, and when the apparatus is well designed and working properly the rate of flow of gas is such that its temperature, as it issues from E, is not much below that of the atmosphere. If we are dealing with gases other than air, which have to be prepared beforehand, there is no reason why the issuing gas should not be taken from E back to the compressor (as indicated by the dotted line extension to E) and used over again, for we are relying on the Joule Thomson effect and not on the external work for the coolings. This is in fact done.

The credit of making use of the Joule Thomson effect is generally attributed to Hampson and Linde, who first independently obtained liquid air without the use of refrigerating agents. Much useful work was done by Dewar, and his vacuum vessels (the origin of thermos flasks) were a most valuable contribution to the problem of heat insulation and the handling of liquefied gases. Kammerlingh Onnes also did much work at this time, and his later work, including the liquefaction of helium (page 292), is classical.

**Liquefaction of Hydrogen.**—Since the Joule Thomson effect for hydrogen above  $-80.5^{\circ}$  C. is positive, i.e. a heating effect, it is

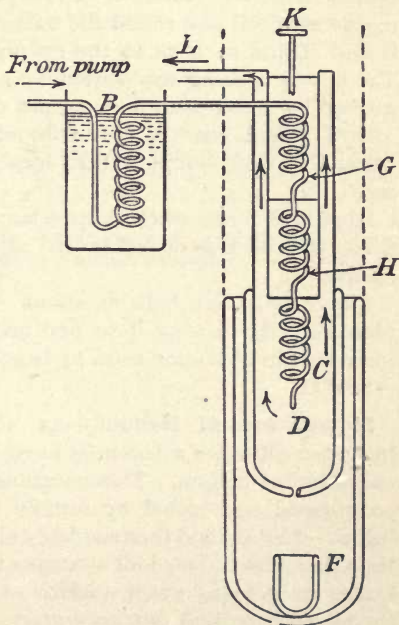


FIG. 129.

is positive, i.e. a heating effect, it is

clear that we cannot begin with hydrogen at atmospheric temperature and expect to liquefy it by this process which depends on internal work. In order to do so the hydrogen must first be cooled well below the inversion point by external means. For this purpose liquid air is used, and the plant shown in Fig. 128 is modified by the addition of the necessary cooling coils. Fig. 129 shows diagrammatically the arrangement used by Travers. The cooling is done in stages. The compressed hydrogen (at 200 atmospheres) passed through the coil B, which was immersed in a mixture of solid  $\text{CO}_2$  and alcohol. It then passed through a coil G surrounded by a vessel which was kept filled with liquid air, and from G to a coil H in a vessel in which liquid air was kept boiling under reduced pressure. The gas was thus cooled to about  $-200^\circ \text{C}$ . It then entered the regenerator coil C and escaped from the nozzle D. The expanded gas passes up over the regenerator coil and round the outside of the vessels surrounding G and H and so back to the supply main and the compressor. The nozzle opening was varied by a specially constructed valve worked by a rod passing down the centre of the coils and fitted with a milled head K. The liquid hydrogen collected in the vessel F. Very complete heat insulation was required throughout.

Improved forms of the apparatus have since been designed in which the coil B is cooled by the returning hydrogen after it has reached L.

Liquid hydrogen boils at about  $-253^\circ \text{C}$ . under atmospheric pressure. By causing it to boil under reduced pressure Dewar succeeded in obtaining solid hydrogen. Solid hydrogen melts at  $-259^\circ \text{C}$ .

**Liquefaction of Helium.**—At the temperature of liquid hydrogen all other substances have become solid with the single exception of helium. This substance remains a gas even when compressed and cooled by rapidly boiling liquid hydrogen (i.e. below  $-260^\circ \text{C}$ .) and then suddenly allowed to expand. For a long time therefore it defied all attempts to liquefy it. Kammerlingh Onnes spent many years working at the problem. He first of all set to work to find out accurately such matters as the critical temperature and the inversion point of the Joule Thomson effect; for helium, like hydrogen, has a positive value for this effect at ordinary temperatures. He did this by determining a large

number of isothermal curves at low temperatures and so deducting the values of  $a$  and  $b$  in Van der Waals' equation. By this means he calculated the critical temperature and also the inversion point, which can be found from a knowledge of the positions of the minimum value of  $pv$ .

The critical temperature was uncertain, as different isothermals did not indicate the same value, but he satisfied himself that at any rate the inversion point was above the temperature of rapidly boiling liquid hydrogen, and so concluded that it ought to be possible to apply the regenerative method successfully.

He designed and made an apparatus on the lines already indicated, using rapidly boiling liquid hydrogen as the refrigerating agent. At 7.30 p.m. on July 10, 1908, liquid helium was seen for the first time, and something like 60 c.c. were obtained in this original preparation. The best commentary on this work is to give Onnes' later values for the constants of this gas:—

Critical temperature,  $-268^{\circ}\text{C}$ .

Boiling point (760 mm.),  $-268.8^{\circ}\text{C}$ .<sup>1</sup>

<sup>1</sup>The standard book on the liquefaction of gases is Travers' *Study of Gases*. A brief account of the liquefaction of helium is given in *Nature*, August, 1908. Much work has been done in recent years and it is to be regretted that there is no recent edition of Travers' or some similar book. Much work on liquefaction was done during the war in the efforts to obtain helium in quantity from certain natural gases for the purpose of filling large airships with this light non-inflammable gas.



## CHAPTER XX

### THE GAS EQUATIONS

The experiments of Joule and Thomson indicate that at ordinary temperatures and pressures the internal work done during expansion by a gas like hydrogen or nitrogen is very small; experiments such as those of Amagat show that in these conditions of temperature and pressure the deviation from Boyle's Law is also small.

If then we assume that a gas exactly fulfils Boyle's Law and that the internal work during expansion is zero, the results we deduce will not be far from the truth when applied to actual gases, and if we require greater accuracy a correction can be applied by using the results of the porous plug experiment and those of Amagat.

A gas which fulfils the two conditions is spoken of as a "perfect gas."

The general equation for a perfect gas is  $pv = RT$  where  $T$  is the absolute temperature and  $R$  a constant. This equation is not the expression of a physical law (other than that of Boyle), but is really only a definition of temperature on the gas scale. The physical law, that of Charles, is that temperatures defined in this way by means of different gases will agree closely with one another. We can apply the reasoning of page 280, to determine the meaning of  $R$ . Suppose we have a mass of gas at a temperature  $T$ , and it is heated at constant pressure  $p$  to a temperature  $T + t$ . If  $C_p$  be the thermal capacity of the gas at constant pressure the heat required will be  $C_p \times t$ . During this process the volume will increase to  $v + v'$  where  $v'$  is given by the relation

$$p(v + v') = R(T + t)$$

$$\text{But } pv = RT$$

$$\therefore pv' = Rt,$$

$pv'$  represents the external work done and so  $Rt$  is equal to the external work.

If the gas were heated at constant volume, no external work would be done and the heat required is  $C_v \times t$ . Since we suppose there is no internal work, the whole of the difference between  $C_p \times t$  and  $C_v \times t$  is accounted for by the external work.<sup>1</sup>

If  $J$  is the mechanical equivalent of heat, we have

$$\begin{aligned} J(C_p \times t - C_v \times t) &= Rt \\ \text{or } J(C_p - C_v) &= R. \end{aligned}$$

Thus  $R$  represents the external work done per unit rise in temperature at constant pressure; it is equal to  $J$  times the difference between the two thermal capacities if these are expressed in ordinary heat units.

It is expressed as so many units of work per degree per unit mass of gas and is thus a constant for each gas, and is spoken of as the gas constant. For example, since 1 gm. of hydrogen occupies 11,130 c.c. at 760 mm. and  $0^\circ\text{C}$ .  $R$  for hydrogen is  $\frac{11,130 \times 76 \times 13.6 \times 981}{273}$  ergs per gm. per degree centigrade.

If the mass is in pounds and the pressure in pounds weight per sq. foot and the volume in cubic feet the value of  $R$  would be in foot-pounds per lb. per degree centigrade. If, however, we take the gram molecule of the gas as our unit the value of  $R$  comes out the same for all perfect gases (see page 303).

**Isothermal and Adiabatic Changes.**—The general equation  $pv = RT$  represents the connection between pressure, volume and temperature of a gas and holds good for all possible variations in condition which a gas may undergo. There are, however, certain particular changes where a special relation holds good in addition to the general equation, and the two most important are isothermal and adiabatic.

**Isothermal Changes.**—If the temperature remains constant, the relation between  $p$  and  $v$  is given by Boyle's Law, i.e.  $pv = \text{constant}$ . This is a particular case of the general equation. Since work is done by the gas when it expands it follows that during an isothermal expansion heat must be supplied to the gas to maintain the temperature at its constant value, and during isothermal compression heat must be abstracted from the gas,

<sup>1</sup> It is assumed that  $C_v$  is independent of the pressure. In the case of actual gases Joly found slight variations.

otherwise the energy supplied to it by the work done during compression would cause a rise in temperature.

**Adiabatic Changes.**—If the gas is isolated, and no heat enters or leaves it during the change the latter is said to be adiabatic. A moment's consideration will show that the change in pressure which results from a given change of volume in an adiabatic transformation will be greater than that which accompanies an equal change in volume in an isothermal one. For suppose we have some gas at a pressure  $p$  and temperature  $T^1$  occupying a volume  $v$ . Let it be compressed adiabatically until the volume is reduced to  $v'$ . Work is done on the gas and therefore (since no heat can leave it) the temperature will be raised. If  $p'$  be the resulting pressure, the product  $p'v'$  will be greater than  $p v$  since the gas is now at a higher temperature. Thus  $p'$  must be greater than that which would correspond to the volume  $v'$  at the original temperature. In the same way, if the gas expands the temperature will fall and the drop in pressure will be greater than that which corresponds to an isothermal change.

**Equation of an Adiabatic for a Perfect Gas.**—The relation between  $p$  and  $v$  for an adiabatic change is given by the equation  $p v^\gamma = \text{constant}$  where  $\gamma$  is the ratio of the two specific heats. This equation can be deduced from energy considerations in the following manner:—

If a gas is heated, and at the same time allowed to expand in any way against external pressure, the amount of heat absorbed by the gas is equal to  $C_v \times \text{rise in temperature} + \text{the thermal equivalent of the external work done}$ . This is a perfectly general relation whether the pressure remains constant or not. Let us consider a very small change so that we may write the external work as  $p \cdot \delta v$ , where  $\delta v$  is the small increase in volume (for a finite change it would be  $\int p \delta v$ ).

We can write the general relation in the form

$$\delta H = C_v \delta T + \frac{1}{J} \cdot p \delta v \text{ where } \delta H \text{ is the heat absorbed}$$

$\delta T$  is the rise in temperature  
and  $\delta v$  the change in volume.

<sup>1</sup> Throughout the remainder of this chapter, whenever temperature is mentioned it represents absolute temperature unless the contrary is stated.

For an adiabatic change  $\delta H = 0$ , and the equation becomes in this case

$$0 = C_v \delta T + \frac{1}{J} \cdot p \delta v \quad \dots \quad (1)$$

Now the complete relation for a gas is the equation

$$pv = RT, \text{ which covers all cases.}$$

If small changes take place in the variables the relation between them is got by differentiating the general equation, and we have for any small change

$$p \delta v + v \delta p = R \delta T \text{ (since } R \text{ is constant)}$$

or 
$$\delta T = \frac{p \delta v + v \delta p}{R} \quad \dots \quad (2)$$

Substitute this value of  $\delta T$  in (1) and we have

$$0 = \frac{C_v}{R} (p \delta v + v \delta p) + \frac{1}{J} \cdot p \delta v \quad \dots \quad (3)$$

But  $R = J(C_p - C_v)$  in all cases (page 295).

Hence (3) can be written

$$0 = \frac{C_v}{J(C_p - C_v)} \{ p \delta v + v \delta p \} + \frac{1}{J} \cdot p \delta v.$$

This form is rather cumbersome; multiply all through by  $\frac{J(C_p - C_v)}{C_v}$ , which is not zero, and we have

$$0 = p \delta v + v \delta p + \frac{C_p - C_v}{C_v} \cdot p \delta v.$$

Now  $\frac{C_p}{C_v}$  is denoted by  $\gamma$ , so that the equation is

$$0 = p \delta v + v \delta p + (\gamma - 1) p \delta v$$

$$\text{or } 0 = v \delta p + \gamma p \delta v.$$

Thus for a small adiabatic change

$$\gamma p \delta v = -v \delta p. \text{ Divide through by } pv \text{ so as to get a form which can be intergrated and we have}$$

$$\gamma \frac{\delta v}{v} = -\frac{\delta p}{p}$$

$$\therefore \gamma \int \frac{dv}{v} = - \int \frac{dp}{p} + \text{an arbitrary constant}$$

$$\text{or } \gamma \log v = - \log p + \text{a constant}$$

$$\therefore \log(v^\gamma) + \log p = \text{constant}$$

$$\therefore pv^\gamma = \text{constant.}$$

The above equation gives the relation between  $p$  and  $v$  for an adiabatic change. The case often arises in which the temperature

variations in an adiabatic change are required. All that is necessary is to make use of the general equation  $pv = RT$ , which is true for all kinds of change. For example, we can substitute for  $p$  the value  $\frac{RT}{v}$ , in which case the equation for an adiabatic becomes

$$\frac{RT}{v} \cdot v^\gamma = \text{constant},$$

or  $Tv^{\gamma-1} = \text{some constant}$  (since  $R$  is constant).

If the relation for  $T$  and  $p$  were required, one would merely substitute  $\frac{RT}{p}$  for  $v$ .<sup>1</sup>

**Experimental Determination of  $\gamma$ .**—The relation for an adiabatic can be used as a means of determining  $\gamma$ ; before Joly's work the value of  $C_v$  was found indirectly by determining  $C_p$  and  $\gamma$ . One of the most perfect forms of an adiabatic change is met with in the propagation of sound waves in a gas. The different portions of the gas suffer alternate compression and rarefaction, and if the pitch of the note is fairly high these compressions and rarefactions take place so rapidly that there is very little chance for any appreciable transference of heat by conduction.

A knowledge of the velocity of sound gives a relation between  $p$  and  $v$  for small adiabatic changes.

It is shown in text-books on sound that the velocity of a compression wave such as constitutes a sound wave is given by

$$\bar{u} = \sqrt{\frac{E}{\rho}}$$

when  $E$  is the elasticity of the material for the particular kind of compression and  $\rho$  is the density.

$E$  is defined as the ratio of the stress to the strain; in the case of compression of a gas the stress is the increase in pressure which we may call  $\delta p$ , and the strain is the fraction of the original value by which the volume is diminished, or  $-\frac{\delta v}{v}$ . The minus sign

<sup>1</sup> In the opinion of the writer it is a mistake for any one to try and remember a large number of formulae and their variations. Nearly all the gas problems can be dealt with by means of  $pv^\gamma = \text{constant}$  (which is the easiest form of the adiabatic equation to remember) and the general equation  $pv = RT$ . It is a poor use for a mind capable of original thought to load it with memorized formulae.



is used because in the ordinary notation of the calculus  $\delta v$  represents the small *increase* in volume, and in our case the volume diminishes when the pressure increases.

Thus  $E = \delta p \div -\frac{\delta v}{v}$  or  $-v \cdot \frac{\delta p}{\delta v}$  which, when the changes are vanishingly small becomes  $-v \cdot \frac{dp}{dv}$ .

For an adiabatic change we have

$$pv^\gamma = \text{constant.}$$

Differentiating with respect to  $v$  we have

$$v^\gamma \frac{dp}{dv} + p \cdot \gamma v^{\gamma-1} = 0$$

or 
$$v \cdot \frac{dp}{dv} + \gamma p = 0.$$

Thus 
$$-v \frac{dp}{dv} = \gamma p.$$

But  $E$  is equal to  $-v \frac{dp}{dv}$ .

Thus for adiabatic compression we have  $E = \gamma p$ .

So that as the propagation of sound waves is a case of adiabatic compressions

$$\bar{u} = \sqrt{\frac{\gamma p}{\rho}}.$$

To illustrate this method let us take the case of air. Experiments show that for dry air at  $0^\circ \text{C}$ .

$$\bar{u} = 33,190 \text{ cm. per second.}$$

If the temperature is constant  $p$  and  $\rho$  vary in the same proportion, so that  $\bar{u}$  is independent of the pressure (for  $\frac{p}{\rho} = \frac{pv}{m}$ , where  $m$  is the mass of the gas).

If  $p = 76 \text{ cm. of mercury} = 76 \times 13.6 \times 981 \text{ dynes per sq. cm.}$

<sup>1</sup> This result represents a solution due to Laplace of a classical difficulty in the theory of sound which remained unsolved for many years. Newton obtained the general result  $\bar{u} = \sqrt{\frac{E}{\rho}}$  for the velocity and then deduced the value for  $E$  by assuming Boyle's Law, which gave  $E = p$ . The velocity of sound thus calculated came out very much lower than the observed values, and the result was an unsolved mystery until Laplace pointed out that the compressions were adiabatic.

1 litre of air weighs 1.293 gms.  $\therefore \rho = .001293$  gms. per c.c.

$$\begin{aligned} \text{Thus } 33,190 &= \sqrt{\frac{\gamma \times 76 \times 13.6 \times 981}{.001293}} \\ \therefore \gamma &= \frac{(33,190)^2 \times .001293}{76 \times 13.6 \times 981} \\ &= 1.406. \end{aligned}$$

The methods of determining the velocity of sound in air are described in elementary text-books of sound; in the case of other gases it is usual to obtain the ratio of the velocity of sound in the gas to that in air by the Kundt's tube method.

**Example of the Use of the Adiabatic Relation.**—A type of the problem which sometimes arises in practical work (and perhaps even more frequently in examination questions) is as follows:—

A quantity of air, for which  $\gamma$  is about 1.41, is suddenly compressed to one-third of its original volume. If the initial temperature of the air is  $15^\circ \text{C}$ ., find its temperature after compression.

Treating the compression as adiabatic, we can make use of the relation  $Tv^{\gamma-1} = \text{constant}$ .

If  $v$  is the original volume of the air, we have the initial temperature as  $288^\circ \text{A}$ .

$$\therefore 288 \times v^{\gamma-1} = \text{constant} = T_1 \times \left(\frac{v}{3}\right)^{\gamma-1}$$

$$\therefore T_1 \cdot \frac{v^{\gamma-1}}{3^{\gamma-1}} = 288 \cdot v^{\gamma-1}$$

$$\text{or } T_1 = 288 \times 3^{\gamma-1}$$

$$\begin{aligned} \therefore \log T_1 &= \log 288 + .41 \log 3 \\ &= 2.6550 \end{aligned}$$

$$\begin{aligned} T_1 &= 451.9^\circ \text{A.} \\ &= 178.9^\circ \text{C.} \end{aligned}$$

Thus the temperature after compression is about  $179^\circ \text{C}$ .

In another type of problem, the pressures might be given. Suppose we have some air at  $15^\circ \text{C}$ . and atmospheric pressure, and it is compressed adiabatically until the pressure is 2 atmospheres.

Taking the equation just given  $Tv^{\gamma-1}$  and substituting from the general equation  $\frac{RT}{p}$  for  $v$ ,

$$\text{We have } T \cdot \left(\frac{RT}{p}\right)^{\gamma-1} = \text{constant} \text{ or } T^\gamma p^{1-\gamma} = \text{constant.}$$

$$\therefore 288^\gamma \times p^{1-\gamma} = T_1^\gamma \cdot (2p)^{1-\gamma}.$$

$$\therefore \left(\frac{T_1}{288}\right)^\gamma = 2^{\gamma-1}$$

$$\text{or } \frac{T_1}{288} = 2^{1-\frac{1}{\gamma}}$$

$$\log T_1 - \log 288 = \log 2 - \frac{1}{\gamma} \log 2$$

$$\therefore \log T_1 - 2.4594 = .3010 - .2133$$

$$\log T_1 = 2.5471$$

$$T_1 = 352.5^\circ \text{ A.} = 79.5^\circ \text{ C.}^1$$

**Some other Methods of Determining  $\gamma$ .**—We must now refer briefly to three methods of determining  $\gamma$ , due respectively to Clémont and Desormes, Lummer and Pringsheim, and Jamin and Richard.

The method of Clémont and Desormes is of interest historically as one of the earliest attempts to measure  $\gamma$ . A modified form of the experiment is as follows:—

A large glass globe A (Fig. 130) is fitted with a wide stop-cock B and a narrow manometer tube C, containing a liquid of very low vapour pressure and preferably of low density; Fleuss pump oil satisfies these conditions. A contains the dry gas at a pressure lightly above that of the external atmosphere. The gas having taken up the temperature of its surroundings, the reading of the manometer is taken. B is then opened so that some gas escapes from A and the pressure falls to atmospheric.<sup>2</sup> B is then

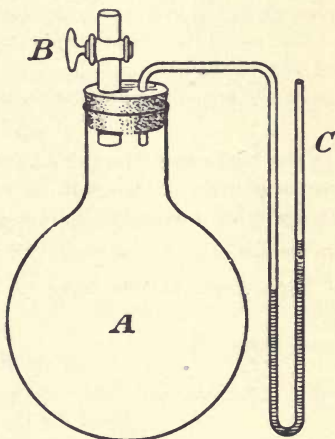


FIG. 130.

<sup>1</sup> It is instructive to compare this heating effect of adiabatic compression with the Joule Thomson effect. With air at this temperature the cooling effect for a drop from 2 atmospheres to 1 atmosphere was about a quarter of a degree. Thus although at high pressures and low temperatures the Joule Thomson effect is sufficiently important to be the basis of gas liquefaction, at ordinary temperatures and pressures it is relatively very small and the error introduced by neglecting it is not serious.

<sup>2</sup> In Clémont and Desormes' method for air the initial pressure was below atmospheric so that air came in when B was opened. This is

immediately closed. The expansion having been rapid, is practically adiabatic, and the gas in A cools slightly. On being left for a time it receives heat from its surroundings, and the temperature returns to the original value; the pressure therefore rises slightly and the final reading of C is noted.

Consider the history of that portion of the gas which does not escape.

Initially it occupies some volume  $v$  rather less than that of the apparatus; it expands adiabatically to  $V$  (that of the apparatus), and finally it receives heat and returns to its original temperature but continues to occupy the volume  $V$  (we neglect the small change in volume due to motion of the liquid in the manometer).

Let  $p_1$  be the initial pressure,  $p_2$  the final pressure, and  $P$  that of the atmosphere.

In the adiabatic expansion we have

$$p_1 v^\gamma = P V^\gamma \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the beginning, the gas occupies a volume  $v$  at pressure  $p_1$ , and at the conclusion, when it has returned to its original temperature it occupies a volume  $V$  at a pressure  $p_2$ .

$$\text{Hence } p_1 v = p_2 V. \quad . \quad . \quad . \quad . \quad (2)$$

$$\text{Thus from (1) we have } \frac{p_1}{P} = \left(\frac{V}{v}\right)^\gamma$$

$$\text{and from (2) } \frac{p_1}{p_2} = \frac{V}{v}.$$

$$\therefore \frac{p_1}{P} = \left(\frac{p_1}{p_2}\right)^\gamma$$

$$\therefore \log p_1 - \log P = \gamma(\log p_1 - \log p_2).$$

$$\therefore \gamma = \frac{\log p_1 - \log P}{\log p_1 - \log p_2}$$

The method is open to various objections. Unless the stopcock is very wide the outrush of gas sets up oscillations and the final state depends on the stage the oscillations have reached when the stopcock is closed. The expansion is probably not truly adiabatic, as the gas is in contact with a large surface of glass; it is noteworthy that even in the improved methods the value of  $\gamma$  comes out low in the case of hydrogen, which is a much better conductor than air.

open to serious objections (see Poynting and Thomson's *Heat*). The method of starting with air at high pressure was first used by Gay Lussac and Welter.

Clément and Desormes' results were low.

The method has been improved by Maneuvrier<sup>1</sup> and by Röntgen,<sup>2</sup> who obtained a good value in the case of air.<sup>3</sup>

**Lummer and Pringsheim.**<sup>4</sup>—This is a modification of the above, in which the fall in temperature of the gas was measured when it expanded adiabatically from  $p_1$  to  $P$ . The calculation for  $\gamma$  then follows as on page 300, from the equation

$$\gamma^\gamma p^{1-\gamma} = \text{constant.}$$

Jamin and Richard<sup>5</sup> adopted the method of supplying by electrical means the same quantity of heat to two equal masses of gas; one was kept at constant pressure and the expansion noted, the other was kept at constant volume and the increase of pressure noted.

They obtained the values 1.41 for air and for hydrogen.

On the whole it may be said that the most reliable methods of obtaining  $\gamma$  are:—

- (1) Direct determination of  $C_p$  and  $C_v$  separately.
- (2) Velocity of sound.

**Relation of  $\gamma$  to the Composition of a Gas.**—We can obtain some insight into this problem by considering the theoretical value of  $\gamma$  on the Kinetic Theory.

First, apart from any question of the kinetic theory, we have the relation of p. 295, that

$$J(C_p - C_v) = R.$$

Let us take as our unit of mass the gram molecule of the gas. To get the value of  $R$  in this case we have:—

Molecular weight in grams of any gas at  $0^\circ\text{C}$ . and 760 mm. occupies 22.4 litres.

Hence from the relation  $pv = RT$  we have:—

$$76 \times 13.6 \times 981 \times 22,400 = R \times 273$$

$$R = 9.318 \times 10^7 \text{ ergs per degree.}$$

Now  $J = 4.18 \times 10^7$  ergs per calorie.

$$C_p - C_v = \frac{8.318 \times 10^7}{4.18 \times 10^7}$$

$$= 2 \text{ calories (approx.)}$$

<sup>1</sup> *Comptes Rendus*, 1895.

<sup>2</sup> *Pogg. Ann.*, 1873.

<sup>3</sup> This sentence shows the view taken by the writer as to the general reliability of the method: it is assumed that the result obtained by other methods is the test of this experiment.

<sup>4</sup> *Ann. der Physik*, 1898.

<sup>5</sup> *Comptes Rendus*, 1870.



If we regard the gas from the kinetic theory and assume that the molecules are simply infinitesimally small particles, the only energy they can have is kinetic energy of translation. Thus if we heat the gas at constant volume, i.e. so that no external work is done, the heat absorbed ( $C_v \times$  rise in temperature) all goes in increasing the kinetic energy of translation. The kinetic energy of each molecule is  $\frac{1}{2}m\bar{u}^2$ , so that of the gas is  $\frac{1}{2}Nm\bar{u}^2$  (page 269).

On the kinetic theory

$$pv = \frac{1}{3} Nm\bar{u}^2.$$

Therefore kinetic energy of the gas is equal to

$$\frac{3}{2} pv.$$

Let us take the molecular weight in gms. of a gas at  $0^\circ$  and 760 mm. and raise its temperature from  $0^\circ$  C. to  $1^\circ$  C. at constant volume.

The gain in kinetic energy will be

$$\frac{3}{2} (\text{change in } pv)$$

$$= \frac{3}{2} \times \frac{1}{273} \times (\text{value of } pv \text{ at } 0^\circ \text{ C. and } 760 \text{ mm.}).$$

$$\therefore C_v = \frac{1}{J} \left( \frac{3}{2} \times \frac{1}{273} \times \text{value of } pv \text{ at } 0^\circ \text{ C. and } 760 \text{ mm.} \right).$$

But in the last paragraph we saw that

$$\frac{1}{J} \times \frac{1}{273} \times (pv \text{ at } 0^\circ \text{ C. and } 760 \text{ mm.}) = 2 \text{ calories.}$$

$$\therefore C_v = \frac{3}{2} \times 2 = 3 \text{ calories.}$$

Thus we should expect  $C_v$  to be 3 calories,  
and  $C_p$  to be 5 calories.

$$\therefore \gamma = \frac{5}{3} = 1.667.$$

In the case of the gases, helium, argon, neon, mercury vapour, which from chemical reasoning are regarded as monatomic, the value of  $\gamma$  found by experiment is very close to this value 1.667.

On the other hand, for gases like air, oxygen, etc., it is about 1.4, and for carbon dioxide 1.29.

If the molecules are not mere particles of infinitesimal size, they might possess kinetic energy other than that of translation ;

for example, if they were groups of atoms the group might have energy of rotation as well as of translation. In that case when the temperature was raised the energy of rotation would probably increase as well as that of translation.<sup>1</sup> We should therefore expect  $C_v$  to be  $3 + m$ , where  $m$  represents the extra energy of rotation;  $m$  would increase with the complexity of the molecule.

But  $C_p - C_v$  remains 2 since this is governed by the external work.

Hence  $\gamma$  would be  $\frac{5 + m}{3 + m}$ , and so would be less than  $\frac{5}{3}$ ; the greater the value of  $m$  the less would be the value of  $\gamma$ . It is found that the more complex the molecule the smaller is the value of  $\gamma$ , so that something of the kind indicated must be going on.

It may be noted that if the molecules be not very complex,  $m$  approximates to the value 2 for each extra atom after the first.

Thus for the monatomic gases, helium, argon, etc.

$$\gamma = \frac{5}{3} \text{ about.}$$

For the diatomic gases, hydrogen, nitrogen, etc.

$$\gamma = \frac{7}{5} \text{ or } 1.4 \text{ about.}$$

For triatomic gases, e.g.  $\text{CO}_2$ , water vapour,  $\text{H}_2\text{O}$ ,

$$\gamma = \frac{9}{7} \text{ or } 1.3 \text{ about.}$$

This is not a strict law, however, and it breaks down at the more complex molecules.

This is a case of the law of distribution of energy between different degrees of freedom (Maxwell).

## CHAPTER XXI

### THERMODYNAMICS

In the chapter on heat engines attention was drawn to the fact that in such engines only a fraction of the heat taken in is converted into useful work, and that there is always a large amount of heat returned to the condenser or the atmosphere. As by far the greater part of the energy needed in carrying out the various requirements of civilization is derived from some form of heat engine, it becomes a matter of the utmost direct practical importance, apart altogether from its value in the development of the theory of heat, to find out the conditions which determine what fraction of the total heat supplied can be converted to work. The present chapter is devoted to the consideration of such conditions and some of the consequences which result from them.

**Work done by an Engine—Indicator Diagrams.**—For our present purpose it is undesirable to confuse the issue by considering the work wasted in friction in the engine itself; we shall therefore deal with the work done by the steam or gas on the piston, and not with the final output as measured by a brake. This is done by using the relation of page 279 for the work done by an expanding fluid; in practice it is accomplished by using an "indicator," an instrument which gives a continuous record of the pressure in the cylinder for every position of the piston in its stroke. The indicator consists essentially of a small cylinder connected to the engine cylinder and fitted with a piston; this works against a spring, so that when the steam (or gas) pressure rises the piston moves up and compresses the spring. The motion of the piston is transmitted through levers to a pencil which presses lightly on a sheet of paper fixed to a drum; the latter rotates backwards and forwards through a certain angle corresponding with the backward and forward motion of the engine piston.<sup>1</sup>

<sup>1</sup> This is usually accomplished by a cord, connected through a reduc-

The curve traced out by the indicator pencil during one complete to-and-fro stroke gives a record of the conditions in the cylinder and is called an indicator diagram. Fig. 131 represents a diagram such as might be obtained. The ordinates represent pressures and the abscissæ which actually correspond to the positions of the piston are proportional to the volume of the contents of the cylinder. The work done by the steam on the piston during the outstroke is equal (page 279) to the area under the curve ABC, i.e. KABCL. The work done by the piston on the steam during the instroke is equal to the area under the curve CDA, i.e. LCDAK. The difference between these two areas, i.e. the area of the closed curve ABCDA, represents the net work done on the piston during one complete to-and-fro stroke. This work, multiplied by the number of revolutions per minute, gives the work done per minute, and so the horse-power.<sup>1</sup>

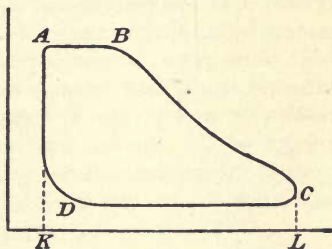


FIG. 131.

The horse-power found in this way is called the Indicated ing lever with the cross head of the piston rod, so that the movements of the drum are a copy on a small scale of the movements of the engine piston.

<sup>1</sup> In actual practice the scale of pressures is known, but the precise ratio of the abscissæ to piston stroke is not. The engineer therefore uses the diagram to determine the "mean effective pressure," i.e. the average value of the difference between the pressure on the out stroke and the pressure on the in stroke. This he does either by measuring the area of the diagram by a planimeter and dividing by the length KL; or by dividing the base into ten or twelve equal parts, erecting perpendiculars from the middle of each part, measuring the lengths of these perpendiculars between the top and bottom line of the diagram, and taking the mean of these lengths. The mean effective pressure multiplied by the area of the piston and multiplied by the length of the stroke gives the work done; this multiplied by the number of revolutions per minute gives the work done per minute. Thus the indicated horse-power is given by  $\frac{PLAN}{33,000}$ , where P is the mean effective pressure,

lbs. sq. inch, L the length of the stroke in feet, A the area of the piston in sq. inches, and N the number of revs. per minute. It will be seen that PLA comes to the same thing as  $\int pdv$  round the closed curve; the question is one of practical convenience.

horse-power, and is written I.H.P. ; if the engine is double-acting a similar diagram must be taken from the other end of the cylinder and the two values added together to get the total work done.<sup>1</sup>

Now in all heat engines, as we saw in Chapter VIII, the idea is to have some substance, called the working substance, which is made to expand by heating it and so does work. In any such operation the principle of the Conservation of Energy holds good, so that if a quantity of heat  $\delta H$  is absorbed by the substance and external work  $\delta W$  is done, the difference between  $W$  and  $J\delta H$  (where  $J$  is the mechanical equivalent of heat) must be represented by a gain in energy of the substance. For example, if we heat some gas at constant pressure, we do a certain amount of external work, and we also increase the kinetic energy of the molecules, and (unless the gas is perfect) increase the internal energy of the gas by separating the molecules against their mutual attractions. If we call the change in the energy of the substance  $\delta E$ , we can say

$$J \cdot \delta H = \delta W + \delta E.$$

This statement is known as the *First Law of Thermodynamics*. It will be seen that it is merely a particular statement of the principle of the Conservation of Energy ; with the corollary that heat is one form of energy.

If we perform a series of operations with the working substance and finally bring that substance back to the same conditions under which it started (pressure, volume, temperature, etc., the same), then the energy of the substance is the same as before, that is to say  $\delta E = 0$ , and the total amount of heat absorbed is equivalent to the total amount of external work done. Such a series of operations is spoken of as a complete cycle. It follows then that if we can perform a complete cycle with our working substance in such a way that on the whole heat is absorbed, such heat is genuinely converted into work, and it is clear that we can go on converting heat to work continuously (so long as the heat is available) by repeating the cycle.<sup>2</sup>

<sup>1</sup> It should be noted that the effective area of the piston for the second diagram is less than that for the first by the area of the piston rod.

<sup>2</sup> It is the necessity for providing for continuous operation that involves the working substance being taken round a complete cycle. In all practical heat engines this is the case : see note on page 105.



It was shown by Carnot in a celebrated essay<sup>1</sup> that the necessary condition for such conversion is that the heat should be "let down from a high temperature to a lower one," that is to say heat should be supplied to the working substance when it is at a high temperature and abstracted from it when it is at a lower temperature; and he showed what form of cycle would result in the greatest possible production of work. This essay is of fundamental importance and is the basis of all engineering practice. It is true that the conditions of Carnot's cycle cannot be completely realized in practice (and incidentally would require an engine to work infinitely slowly); nevertheless the cycle is of supreme importance as giving the ideal standard to be reached and as indicating the way in which it may be approached.

The following account of Carnot's reasoning differs in one point from the original (see footnote, page 312); to retain the earliest form at this stage would only obscure the issue.

**Reversible Processes.**—In all the operations which occur in Carnot's cycle the process must be reversible. Reversible, in the thermodynamic sense, means that at every stage of the process an infinitesimal change in the external conditions will make it go the other way. We may illustrate this by considering a simple case. Let Fig. 132 represent a long metal cylinder fitted with a frictionless piston and containing some water. The whole is placed in a constant-temperature bath. Let  $p$  be the vapour pressure of water at the temperature of the bath, and  $A$  be the area of the piston. If the piston be loaded so that the total weight of it is  $pA$ , nothing will happen. But if the load be diminished ever so slightly, the water under the piston will begin to evaporate, pushing it up, and at the same time will absorb the necessary latent heat of evaporation from the bath. This process can go on until all the water has turned to vapour. If at any stage the load is increased so that it is slightly greater than  $pA$ ,

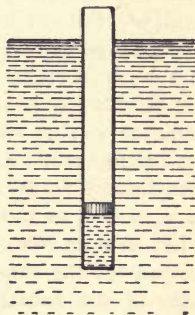


FIG. 132.

<sup>1</sup> Sadi Carnot, *Réflexions sur la puissance motrice du feu et sur les moyens propres à la développer*, 1824. An English translation by R. H. Thurston is published by Macmillan & Co.

the piston will descend, vapour will condense, and latent heat of evaporation will be given up to the bath. Thus by changing the load from an amount infinitesimally less than  $pA$  to one infinitesimally greater the whole operation has been made to go the other way. It would be difficult in practice to carry out a corresponding process in the case of a gas at constant temperature; to do this we should have to alter the load on the piston from moment to moment so that at every stage it was infinitesimally less or greater (as the case might be) than the force due to the gas. Nevertheless we can conceive such a process.

A little thought will show that in both these cases the movement of the piston would have to be indefinitely slow, otherwise finite differences in pressure would arise.

**Carnot's Cycle.**—The working substance can be anything (provided that it does change in volume when heated), but it is easiest to picture it as a gas or vapour. Imagine it contained in a cylinder, fitted with a frictionless piston. The piston and the walls of the cylinder are made of material which is a perfect heat insulator, but the base is of a perfect conductor. The whole can be placed at will on either X, Y, or Z (Fig. 133). X is a source of heat which remains at a constant temperature  $\theta_1$ , and can supply any quantity of heat required. Y is a stand of some perfect heat insulator, so that when the cylinder is placed upon it, the contents can neither receive nor give out heat. Z remains at a constant temperature  $\theta_2$ , and can absorb any quantity of heat. We shall refer to this as the sink.

Let us start with the working substance at  $\theta_2$ ; the volume will depend on the mass of substance in the cylinder. The initial state of the substance is represented by the point A on the indicator diagram. Place the cylinder on Y and gradually increase the load on the piston so that the substance is compressed by a reversible process. As the cylinder is on Y, there is complete heat insulation, and the process is adiabatic; the temperature of the working substance will rise. Let the compression go on until the temperature has reached  $\theta_1$ . AB on the indicator diagram represents this part.

Now place the cylinder on X, and by adjusting the load allow the working substance to expand reversibly and isothermally. Let this go on until the substance has reached some suitable condition, represented by C on the indicator diagram. Transfer

the cylinder to Y and allow the expansion to continue reversibly : it will now be adiabatic and the temperature will fall. CD represents this part of the operation. When the temperature of the working substance reaches  $\theta_2$ , place the cylinder on Z and alter the load so that the substance is compressed reversibly and isothermally ; DA represents this part. During the compression heat will be given up to the sink. Continue the process until the substance reaches the condition represented by A ; we have now

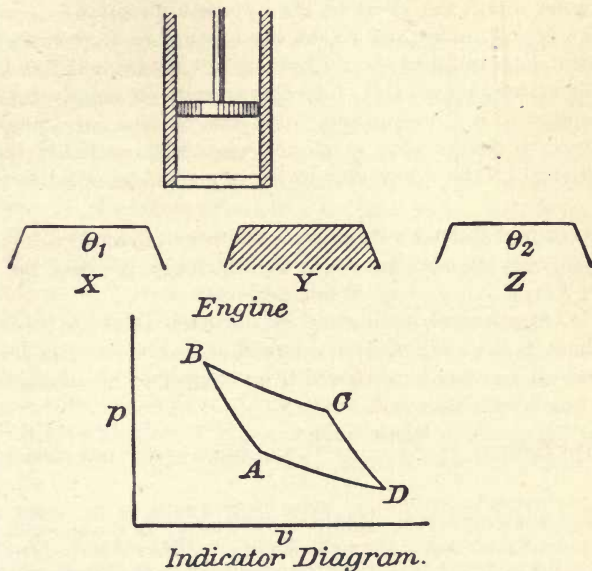


FIG. 133.

completed the cycle, and the conditions are the same as when we started.<sup>1</sup>

During the cycle work is done by the substance along BC and CD, and work is done on it along DA and AB. The net work done by the working substance is, as already explained, equal to the area of the indicator diagram. During the isothermal expan-

<sup>1</sup> A is the most suitable point at which to start the cycle, since it is easy to know when we have got back to it. If we start at B we have got to carry on our isothermal compression to such a point that if the adiabatic compression takes place we shall just hit off the point B.

sion the substance takes in a quantity of heat  $H_1$  from the source X, and during isothermal compression it gives up heat  $H_2$  to the sink Y; the other parts of the cycle are adiabatic, so no heat transfer occurs. Since the working substance returns to its initial condition, the First Law of Thermodynamics tells us that  $J(H_1 - H_2) = \text{external work done} = \text{area of indicator diagram}$ .<sup>1</sup>

It is clear also that, since every operation is reversible, we could have gone round the cycle in the opposite direction; in which case we should have had to do work equal to the area of the indicator diagram, and should have taken  $H_2$  from the sink and put the greater amount  $H_1$  into the source. If this is done the engine acts as a "heat pump" and the process corresponds to the action of refrigerating machines (page 166), and also (though less closely) to the operations in the liquefaction of gases (page 290).

**Efficiency of Carnot's Process.**—The function of a heat engine being to convert heat to work, the efficiency is given by

$$\frac{\text{Work done}}{\text{Mechanical equivalent of the heat absorbed}}$$

That heat is also rejected is interesting, but of no use for our purpose—it represents heat which we wished to be converted to work but which was not.

Thus efficiency =  $\frac{\text{Work done}}{J \times H_1}$ , and since we are not considering

<sup>1</sup> In his original essay, Carnot based his reasoning on the conservation of energy, but adopted the caloric theory of heat; he therefore assumed that the heat given up to the sink was equal to that absorbed from the source; the process of dropping from the high to the low temperature enabled it to do work. This idea of heat rather corresponds to the case of an electric motor: in this the current flowing out is equal to the current flowing in and the work is done by the electricity dropping from the high potential to the low. The later experiments of Joule and especially of Hirn showed that the heat rejected by an engine is less than that absorbed by an amount proportional to the work done. Thus, as summarized in the First Law, heat in its own right represents a form of energy apart from all questions of temperature. Nevertheless Carnot's argument remains valid as to the availability of heat for doing work; it was modified by Clausius and by Lord Kelvin to accord with the dynamical theory of heat.

It may be pointed out that Carnot implies that he does not commit himself as to the nature of heat and adopts the caloric idea as a possible view. Before the close of his short life in 1832 he appears to have had a clear appreciation of heat as a form of energy.



friction losses in the engine we can put  $J(H_1 - H_2)$  for the work done.

$$\text{Thus efficiency} = \frac{J(H_1 - H_2)}{J \times H_1} \text{ or } \frac{H_1 - H_2}{H_1}.$$

This is only expressing the efficiency as the fraction of the whole heat absorbed which is converted to work.

The next proposition is to show that *No engine working between the same two temperatures can be more efficient than a reversible engine.*

Suppose we have a reversible engine working between a source at  $\theta_1^\circ$  and a sink at  $\theta_2^\circ$ ; let it take an amount of heat  $H$  from the source per cycle and do work  $W$ . If we have a more efficient engine working between the same source and sink, it means that if it absorbs  $H$  from the source per cycle it can do more work than  $W$ . Let this engine be arranged to drive the reversible one backwards; the latter then acts as a heat pump, delivering heat  $H$  to the source per cycle and requiring work  $W$  to be done on it. Now the efficient engine can do more than  $W$  per cycle, so that it can drive the other and do some other work as well. But it only takes  $H$  from the source per cycle, so that one engine returns as much heat as the other absorbs. Thus the combined engines take no heat from the source, but are able to do a certain amount of extra work per cycle; the process can go on indefinitely. By the First Law of Thermodynamics the heat equivalent of this work must have come from somewhere; it must therefore have come from the sink.<sup>1</sup>

We could, if we liked, have arranged that our more efficient engine did an amount of work  $W$  just sufficient to drive the reversible engine; in that case it would absorb an amount of heat  $H'$  from the source somewhat less than  $H$ . The combined engines would then do no extra work, but an amount of heat  $H - H'$  would be transferred to the source each cycle, and this heat must have come from the sink.

Thus by a continuous process, and without external aid, we

<sup>1</sup> In Carnot's essay since the heat rejected by an engine was assumed to be equal to that absorbed, it followed that no heat came from the sink either, and this involved continuous work without absorption of energy—in other words "perpetual motion." It was therefore regarded as a proof of impossibility. This argument does not apply when we adopt the dynamical theory of heat, but the general conclusion remains the same if we adopt the Second Law of Thermodynamics.



should be able either to obtain work by absorbing heat from the low-temperature sink, or cause heat to pass from the cold body to the hot. As far as the First Law of Thermodynamics is concerned this might be possible; but it is contrary to all experience that either of these things should happen. This statement is put forward in the hypothesis which is known as the *Second Law of Thermodynamics*, and is usually expressed in one of two forms, which really come to the same thing. "It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of surrounding objects."

This form is Kelvin's method of expression.

Clausius puts it in the form: "It is impossible for a self-acting machine, unaided by external agency, to convey heat from one body to another at a higher temperature, or heat cannot of itself pass from a colder to a warmer body."

It is important to notice that this law applies only to continuous operations—e.g. some compressed gas when released from pressure will do work and cool itself, but this cannot go on indefinitely, and further the gas must originally have been compressed by external agency. The Second Law is not capable of direct proof, but we are convinced of its truth because no experiment has ever succeeded in disproving it and predictions based on it are found to be correct.

Once the Second Law is admitted it follows that no engine can be more efficient than a reversible engine working between the same temperatures. It follows also that all reversible engines are equally efficient whatever the working substance; for if one is more efficient we can set it to drive the other backwards and get the results of the previous paragraph. The only condition which affects the efficiency of a reversible engine is the temperatures at which it takes in and rejects heat; we must now see in what way the efficiency depends on the temperature.

It is important to remember that the results of the last paragraph make the following reasoning quite general; since no engine can be more efficient than a reversible engine we can take the Carnot cycle and any working substance which is easy to follow and apply the results to other cases.

The working substance takes in heat during the process repre-

sented by the isothermal BC (Fig. 134); the amount taken in is clearly determined by conditions implied by BC, and is not influenced by any subsequent operations. How much of this heat is converted into work depends on the area of the indicator diagram; in fact the possibility of any work being done at all during the cycle depends on DA being below BC, so that during the return stroke the pressure on the piston at any stage is less than the pressure on the corresponding stage in the outstroke. The more we can keep down this back pressure, the more work will be done in the cycle, and this means we must keep the temperature as low as possible. Thus the lower we keep the temperature during the period when heat is taken back from the working substance<sup>1</sup> the greater will be the amount of work done in the cycle. For example, if we return along the isothermal D'A', which represents a higher temperature than AD (for the pressure corresponding to any value of  $v$  is higher along D'A' than DA), the total work done will be represented by the area BCD'A' instead of BCDA.

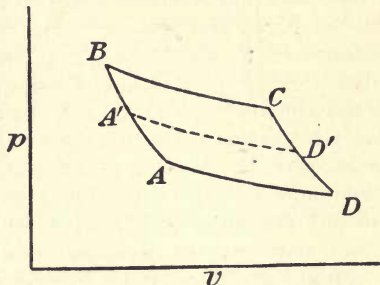


FIG. 134.

We thus arrive at the very important result that if an engine takes in heat at a particular temperature  $\theta_1$ , and rejects heat at a temperature  $\theta_2$ , the fraction of the heat taken in which can be converted into work becomes greater as the temperature drop  $\theta_1 - \theta_2$  is increased.

In practical engines, there is a limit to the lower temperature, which cannot very well be lower than atmospheric (and is usually higher). The only chance of making the efficiency as high as possible is to arrange to take in heat at as high a temperature as possible. The upper limit of temperature is decided by questions of mechanical conditions, and to a large extent by the difficulty of arranging for lubrication at high temperatures. It follows

<sup>1</sup> It is clear that heat must be absorbed during some part of the return stroke, otherwise we shall return along the adiabatic DC.

also that if heat is taken in at any part of the cycle where the temperature is below the maximum, that heat is less advantageously employed; and any heat rejected above the minimum temperature is disadvantageous.<sup>1</sup>

Thus the best possible cycle is that of Carnot, where the heat is all taken in at the highest temperature and rejection of heat takes place at the lowest, the other processes being adiabatic.\*

**Lord Kelvin's Absolute Scale of Temperature.**—The results of the last paragraph give us a means of defining a scale of temperature which is independent of the properties of any particular substance, and of obtaining a conception of the absolute zero of temperature which has a real physical meaning. For if any reversible engine takes in a quantity of heat  $H$  at any particular temperature the fraction of this heat converted into work during a complete cycle will depend only on the temperature of the sink, and will be greater the lower this temperature is made. Now the utmost effect we can conceive (unless we abandon the First Law of Thermodynamics) is to convert the whole of this heat into work; thus if we reduce the temperature of the sink until the

<sup>1</sup> For example, one trouble with steam engines is that some of the steam entering the cylinder is condensed on the relatively colder walls of the cylinder. As the pressure falls towards the end of the expansion stroke re-evaporation takes place, so that some of the heat lost at the beginning returns to the working substance; nevertheless this heat, being taken at a lower temperature, is less available for conversion to work. It was an important point in Watts' engine that the cylinder was jacketed with boiler steam which largely prevented this condensation. It will be seen that it is worse than useless to jacket the cylinder with steam from the exhaust, which is at the lowest temperature.

<sup>2</sup> In actual engineering practice, about the nearest approach to this cycle is met with in the Diesel engine. This is a four-stroke oil engine, which on the induction stroke takes in air only. This is compressed on the compression stroke and the temperature is raised to a high value; oil is pumped into the cylinder in the early stages of the working stroke and at once ignites owing to the high temperature of the air. Thus heat is taken in by the working substance at nearly constant pressure and slightly rising temperature during the first part of the stroke; the oil is then cut off and the contents of the cylinder expand for the rest of the stroke and are then let out by the exhaust valve during the fourth stroke. The thermal efficiency of this engine, judged by its indicated horse-power, is about  $\cdot 4$ , which is higher than other oil engines and something like twice that of the best steam engines. The mechanical efficiency is rather low, so that the thermal efficiency judged from the B.H.P. is about  $\cdot 32$ , which is much the same as the best oil engines, but considerably higher than steam.

whole of the heat taken in is converted to work we have got to the lowest conceivable temperature—an absolute zero in the strictest sense. (It must be again emphasized that we are dealing throughout with complete cyclical operations, so that no work is got from the intrinsic energy of the working substance.) If the temperature of the sink is higher than this absolute zero, the fraction of the heat converted into work, or in other words the difference between the heat absorbed and the heat rejected will depend simply on temperature of the source and sink and on nothing else. On the absolute thermodynamic scale temperatures are therefore *defined* as follows: <sup>1</sup> if a reversible engine takes in a quantity of heat  $H_1$  at one temperature  $\theta_1$  and rejects a quantity  $H_2$  at the lower temperature  $\theta_2$ ,

$$\frac{\theta_1}{\theta_2} = \frac{H_1}{H_2}$$

and in the particular case we have just considered, when  $H_2 = 0$ ,  $\theta_2$  also = 0.

The scale of temperature defined in this way is called the absolute thermodynamic scale and is due to Lord Kelvin.<sup>2</sup>

The thermodynamic scale is of immense importance, since for the first time we have obtained a scale which does not depend on the properties of any arbitrary substance. We must now see how it is related to scales of temperature defined in other ways. For this purpose we will compare it with the perfect gas scale by considering the indicator diagram when a perfect gas is taken

<sup>1</sup> See note at the end of the chapter.

<sup>2</sup> The idea of obtaining an absolute scale of temperature by making use of Carnot's principle was first put forward by Lord Kelvin (William Thomson as he then was) in a paper in *Proc. Camb. Phil. Soc.*, reprinted in the *Phil. Mag.*, 1848. In this first paper he adopted the notion of Carnot's essay of 1824 that heat did not disappear and that work was done by the passage of heat from high to low temperature without change in the quantity. Indeed he says "the conversion of heat (or caloric) into mechanical effect is probably impossible," but adds a footnote: "This opinion seems to be nearly universally held by those who have written on the subject. A contrary opinion has been advocated by Mr. Joule of Manchester." Later on he modified his views, and his clear conception of the universal importance of the doctrine of the conservation of energy and the development of its consequences is perhaps the greatest of his contributions to the advancement of knowledge. This may be seen in his collected papers. The history of the absolute scale is of interest as showing how the Second Law of Thermodynamics is an entirely distinct proposition and does not in any way follow from the First.

round a Carnot cycle. It must be remembered that a perfect gas satisfies the following conditions:—

- (1) No internal work is done when the volume changes.
- (2) The gas obeys Boyle's Law exactly at all temperatures.

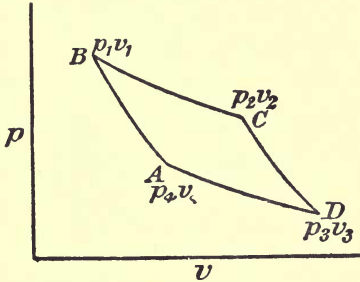


FIG. 135.

Temperature on the perfect gas scale is defined by the relation  $pv = RT$  where  $R$  is a constant and  $T$  the temperature defined in this way.

Let ABCD (Fig. 135) represent the indicator diagram for the perfect gas taken round a Carnot cycle. AB and CD are adiabatics and BC and DA isothermals. Let the temperature of BC defined on the gas scale be  $T_1$  and defined on the thermodynamic scale be  $\theta_1$ . Let AD be  $T_2$  or  $\theta_2$ . Let  $H_1$  be the heat taken in along BC and  $H_2$  the heat rejected along DA.

Now since no internal work is required to separate the molecules of the gas, and there is no rise in temperature along BC, we have  $J \times H_1 =$  external work done by the gas in passing from B to C. Similarly

$J \times H_2 =$  external work done on the gas in passing from D to A. Thus  $J \times H_1 = \int p dv$  along BC.

But for the isothermal BC we have  $pv = RT_1, p = \frac{RT_1}{v}$

$$\therefore J \times H_1 = RT_1 \int_{v_1}^{v_2} \frac{1}{v} dv$$

$$= RT_1(\log_e v_2 - \log_e v_1) = RT_1 \log_e \frac{v_2}{v_1}$$

Similarly  $J \times H_2 = RT_2(\log_e v_3 - \log_e v_4) = RT_2 \log_e \frac{v_3}{v_4}$

$$\therefore \frac{H_1}{H_2} = \frac{T_1 \log_e \frac{v_2}{v_1}}{T_2 \log_e \frac{v_3}{v_4}} \dots \dots \dots (1)$$



Now to find the relation between  $v_1, v_2, v_3, v_4$  we have from the adiabatics

$$p_1 v_1^\gamma = p_4 v_4^\gamma \text{ and } p_2 v_2^\gamma = p_3 v_3^\gamma$$

or

$$\frac{p_2 v_2^\gamma}{p_1 v_1^\gamma} = \frac{p_3 v_3^\gamma}{p_4 v_4^\gamma} \quad \dots \quad (2)$$

and from the isothermals we have

$$p_1 v_1 = p_2 v_2 \text{ and } p_3 v_3 = p_4 v_4$$

or

$$\frac{p_1 v_1}{p_2 v_2} = 1 = \frac{p_4 v_4}{p_3 v_3} \quad \dots \quad (3)$$

If we multiply equations (2) and (3) we shall eliminate the  $p$ 's and obtain

$$\left(\frac{v_2}{v_1}\right)^{\gamma-1} = \left(\frac{v_3}{v_4}\right)^{\gamma-1}$$

or

$$\frac{v_2}{v_1} = \frac{v_3}{v_4}$$

Thus in equation (1) we have  $\log_e \frac{v_2}{v_1} = \log_e \frac{v_3}{v_4}$

and therefore  $\frac{H_1}{H_2} = \frac{RT_1}{RT_2}$  or  $\frac{H_1}{H_2} = \frac{T_1}{T_2}$ .

But  $\theta_1$  and  $\theta_2$  are defined by the relation

$$\frac{\theta_1}{\theta_2} = \frac{H_1}{H_2}$$

Therefore

$$\frac{\theta_1}{\theta_2} = \frac{T_1}{T_2}$$

and since the isothermals were selected quite arbitrarily we have the proposition of fundamental importance that *The thermodynamic scale coincides with the perfect gas scale.*

Now Callendar and others<sup>1</sup> have shown how to calculate the value of a temperature measured on a hydrogen or nitrogen thermometer in terms of the perfect gas scale from a knowledge of the deviation from Boyle's Law and the porous plug experiment.

Thus it is possible actually to measure any particular temperature and then obtain its value on the thermodynamic scale which is independent of the properties of any substance and depends only on the laws of energy.

It may be pointed out that since the deviations of the hydrogen and nitrogen scales from the perfect gas scale are very small, and practical temperature measurements up to 1,600° C. are

<sup>1</sup> Cp. Preston's *Theory of Heat*, 3rd edition.

based on one or other of these two scales, it is sufficient in engineering practice to say that the limit for the efficiency of any engine is given by the relation

$$\frac{H_1 - H_2}{H_1} = \frac{T_1 - T_2}{T_1}$$

where the temperature is measured in the ordinary way, but, of course, expressed as degrees Absolute, not degrees Centigrade.

**Note on the Definition of Temperature on the Thermodynamic Scale.**—In the account of the thermodynamic scale it was stated that temperatures were defined by the relation  $\frac{\theta_1}{\theta_2} = \frac{H_1}{H_2}$ ; it is convenient to give in a more concise form the detailed reasoning which shows that the definition of temperature in this way gives a scale which is perfectly consistent. The following treatment appears to the writer to be the clearest, and has been used by him for a good many years.

Let a reversible heat engine work between two temperatures  $\theta_1$  and  $\theta_2$  defined in any arbitrary way.

The efficiency of the engine, which is given by  $\frac{H_1 - H_2}{H_1}$  (see page 313) depends only on  $\theta_1$  and  $\theta_2$ ; we can express this by the relation

$$\frac{H_1 - H_2}{H_1} = f(\theta_1, \theta_2) \text{ where } f(\theta_1, \theta_2) \text{ is some function of } \theta_1 \text{ and } \theta_2$$

whose form is determined by the way in which the temperatures are defined.

We can write this relation in the form

$\frac{H_1}{H_2} = \varphi(\theta_1, \theta_2)$  where  $\varphi(\theta_1, \theta_2)$  is some other function of  $\theta_1$  and  $\theta_2$  related to  $f(\theta_1, \theta_2)$  by the condition that since

$$\frac{H_1 - H_2}{H_1} = 1 - \frac{H_2}{H_1} \quad f(\theta_1, \theta_2) = 1 - 1/\varphi(\theta_1, \theta_2).$$

Let a second reversible engine work between  $\theta_2$  and  $\theta_3$ , and let it be of such a size that it takes in  $H_2$  at  $\theta_2$  per cycle.

Then as before the efficiency =  $f(\theta_2, \theta_3)$ ,

and 
$$\frac{H_2}{H_3} = \varphi(\theta_2, \theta_3).$$

If now the engines are arranged to work as a single engine and the strokes are timed so that as the first rejects its heat  $H_2$  the second takes in the  $H_2$ , we have a single reversible engine in

which the working substance happens to be contained in two cylinders; this engine takes in heat  $H_1$  at  $\theta_1$  and rejects  $H_2$  at  $\theta_2$  and therefore

$$\frac{H_1}{H_2} = \varphi(\theta_1, \theta_2).$$

But by ordinary multiplication

$$\frac{H_1}{H_2} \times \frac{H_2}{H_3} = \frac{H_1}{H_3}$$

$$\therefore \varphi(\theta_1, \theta_2) \times \varphi(\theta_2, \theta_3) = \varphi(\theta_1, \theta_3).$$

If then  $\theta_2$  disappears when  $\varphi(\theta_1, \theta_2)$  is multiplied by  $\varphi(\theta_2, \theta_3)$  it means that the form of the function must be a fraction in which some function of  $\theta_1$  occurs in the numerator and the same function of  $\theta_2$  in the denominator, or

$$\varphi(\theta_1, \theta_2) = \frac{\psi(\theta_1)}{\psi(\theta_2)}$$

$$\text{i.e.} \quad \frac{H_1}{H_2} = \frac{\psi(\theta_1)}{\psi(\theta_2)}.$$

Thus, however we define  $\theta$ , we can get a consistent scale of temperature provided that we define it in such a way that

$$\frac{H_1}{H_2} = \frac{\text{some function of } \theta_1}{\text{the same function of } \theta_2}.$$

The function  $\psi(\theta)$  can be of any form we choose.

The simplest way is to define  $\theta$  so that  $\psi(\theta)$  is simply  $\theta$ ; we arrive at a consistent scale by defining it in such a way that

$$\frac{H_1}{H_2} = \frac{\theta_1}{\theta_2}.$$

## CHAPTER XXII

### TRANSFORMATION OF ENERGY—DEGRADATION AND DISSIPATION OF ENERGY—ENTROPY

**Conservation of Energy and the First Law of Thermodynamics.**—During the latter half of the nineteenth century, the researches of Joule, Hirn and others, and particularly the work of Lord Kelvin, placed on a firm foundation the exceedingly important Principle of the Conservation of Energy. This principle may be stated in the form that there is some identity underlying the phenomena of mechanics, heat, light, electricity, etc. These phenomena are different manifestations of something which we call energy. The different forms are mutually convertible, that is to say if we have the power to produce certain phenomena in light and this in some way disappears, there is left in place of it the power to produce certain phenomena in heat or electricity or mechanics, as the case may be. Moreover there is a definite numerical relation between the capacity to produce the optical phenomena measured in suitable units, and the capacity to produce the phenomena in heat which appears in place of it. Energy cannot be created or destroyed; if one form of it disappears a corresponding amount in another form appears. This general principle is the Principle of the Conservation of Energy; the First Law of Thermodynamics is a particular part of it which says that heat as measured in ordinary thermal units is one of the forms of Energy. Put in its simplest form, the First Law of Thermodynamics is given by the relation  $J \times H = W$  where  $H$  is a quantity of heat,  $W$  the work done when  $H$  disappears (and no other form of energy comes into the question) or the quantity of work which disappears when  $H$  is produced, and  $J$  a constant depending on the units chosen to measure  $H$  and  $W$ .

Since however there might be an appearance or disappearance of other forms of energy besides mechanical work, the most



general statement of the principle is that of page 308, namely

$$J \times \delta H = \delta W + \delta E.$$

**Distinction between Heat Energy and other Forms. The Second Law of Thermodynamics.**—Although the different forms of energy are equivalent in the sense that they can all be expressed in terms of a common standard, and that if a certain quantity of one form disappears a corresponding quantity of another form appears somewhere, there is an important distinction between heat energy and other forms. We can carry out, or conceive of, processes by which one of these latter forms can be completely converted into another, or any form can be converted into heat; but there is a limitation on our powers of converting heat into other forms.

It has been shown in the last chapter that heat can only be converted to mechanical work when it is let down from a body at high temperature to one at a lower temperature, and that even when the circumstances are most favourable, i.e. all the operations are reversible in the thermodynamic sense, the whole of the heat is not converted to work unless the sink is at the absolute zero of temperature. If then we have an isolated system possessing heat energy, and all parts of the system are at the same temperature, none of the heat energy can be converted to mechanical energy. It is thus apparent that there is a distinction between heat energy and other forms in that we can never convert the whole quantity of heat into work, and in some cases we cannot convert any of it.

It is conceivable that this distinction is due to our own limitations rather than to a fundamental difference in the nature of the energy. If we regard heat energy as the kinetic energy of the ultimate particles of matter the limitation means that we are unable to isolate the particles and direct their kinetic energy so that it may be available for our own particular purpose. Whether this is so or not, we must regard heat energy as a lower grade than other forms in that we have not a free choice in the use of such energy. It should be noted that this proposition is in no way a consequence of the Principle of the Conservation of Energy; indeed the first recognition of it was founded on a train of reasoning which involved a violation of that principle. The proposition is expressed in the *Second Law of Thermodynamics* which is to be found stated in many different forms, but which practically comes



to a quantitative statement of the distinction between heat energy and other forms.

**Degradation and Dissipation of Energy.**—If we have a system of which some parts are at a higher temperature than others we can convert some of the heat energy into work by using a reversible engine which takes in heat from the hot parts and rejects a portion of it to the cold. On the other hand, if heat passes directly, e.g. by conduction, from the hot parts to the cold, such heat is no longer available for conversion to work. In this case the system is said to have suffered a degradation of energy since its energy is now less available. There is a constant tendency for heat to pass from places at high temperature to those at lower temperatures, thus bringing about this degradation of energy. Again in any actual conversion of energy from one form to another there is always a certain amount wasted in such ways as friction, turbulent motion of fluids, electrical resistance, etc., the wasted energy being converted to heat. This conversion by the way of a portion of the energy into heat is spoken of as the dissipation of energy.

Thus although the total amount of energy in an isolated system remains constant, and any changes which occur merely alter the form of the energy and not its amount, yet in any such change there will be a certain amount of dissipation of energy into heat. And whether changes occur or not there is a tendency for heat to pass from places at high temperature to those of lower temperature; there is no known method of complete heat insulation. Thus in addition to the Principle of the Conservation of Energy we have the very important practical Principle of the degradation and dissipation of energy which tells us that the energy of a system is always tending to become less available for general use.

**Entropy.**—We must now deal with a conception which is of great use to the engineer in calculations of the behaviour of heat engines and which has many applications in physical problems. We have seen that Carnot, in his essay of 1824, regarded his engine as rejecting the same amount of heat as it took in, the work being done by the heat dropping from a high temperature to a low: this conception is rather like the case of a water motor where the quantity of water which comes out of the waste pipe is equal to that which flows in, work being done because the pressure of the water on the inlet side is greater than that on the

outlet. It is now established that this is not the case with a heat engine; some heat disappears, and there is a conversion of heat to work. The conception of the physical quantity known as entropy does provide us with something which under certain conditions may be regarded as passing through the heat engine just as the water passes through the water motor or the electric current through an electro-motor without altering in amount. We will first define entropy and then consider its meaning.

*Definition.*—If a substance at a temperature (absolute)  $\theta$  absorbs a quantity of heat  $H$  it is said to receive an amount of entropy  $\frac{H}{\theta}$ . If the temperature does not remain constant during the process we must divide the quantity of heat into small elements  $\delta H$  such that during the absorption of each element the temperature remains practically constant and regard the entropy received as  $\int \frac{dH}{\theta}$ .

Consider the system made up of a source at  $\theta_1$ , a sink at  $\theta_2$ , and a Carnot engine working between them. During the outstroke, the source gives up an amount of heat  $H_1$  to the working substance. It therefore gives out an amount of entropy  $\frac{H_1}{\theta_1}$ , and the working substance receives entropy  $\frac{H_1}{\theta_1}$ .<sup>1</sup>

While the working substance is expanding adiabatically it neither absorbs nor rejects heat, and so it neither gives nor receives entropy. On the instroke the working substance rejects  $H_2$  at  $\theta_2$ , and so it gives out entropy by  $\frac{H_2}{\theta_2}$ ; at the same time the sink takes in  $H_2$  at  $\theta_2$  and so receives entropy  $\frac{H_2}{\theta_2}$ . During adiabatic compression there is again no change of entropy.

But in a Carnot cycle  $\frac{H_1}{\theta_1} = \frac{H_2}{\theta_2}$ . Hence the entropy lost by the source is equal to that gained by the sink, and the entropy taken in by the working substance is equal to that which it rejects. Thus for the system as a whole there is

<sup>1</sup> Since the operation is reversible the temperature of the working substance while it is taking in heat is indefinitely near that of the source so that  $\theta$ , refers to both of them.

no change of entropy; a certain amount has been transferred from the source to the sink, passing through the engine on the way, just as a current passes from the high potential side to the low potential through an electro-motor.

**The Entropy of a System tends to increase.**—The analogy between entropy and quantities such as quantity of electricity must not be pushed too far; entropy has the distinctive property that it tends to increase. For suppose we have some part of a system at a temperature  $\theta_1$ , and a quantity of heat  $\delta H$  passes directly from it to a part at a lower temperature  $\theta_2$ . The hot part loses entropy  $\frac{\delta H}{\theta_1}$  and the cold part receives entropy  $\frac{\delta H}{\theta_2}$ ; the cold part therefore receives more entropy than the hot part loses, so that the entropy of the system is increased. Again, if there is any dissipation of energy through friction, this energy is converted to heat and there is a gain of entropy  $\frac{H}{\theta}$  where  $\theta$  is the temperature of the part receiving the heat, and no corresponding loss of entropy in other parts. Both of these effects tend to happen, and so there is a tendency for the entropy to increase.

We have just seen that if some of the heat energy is converted to work by a reversible process the entropy of the system does not change, for  $\frac{H_1}{\theta_1} = \frac{H_2}{\theta_2}$ . By no process can we make  $\frac{H_2}{\theta_2}$  less than  $\frac{H_1}{\theta_1}$ , for if we did we should have converted a greater fraction of  $H_1$  into work than a reversible engine can do. Thus for any isolated system the only possible changes are those which result in the entropy either remaining the same or increasing. It follows also that if the entropy increases some of the energy which might have been available for doing useful work has been degraded into the less available heat.

**Calculation of the Entropy of a Substance.**—Although the change in the entropy of a substance which is receiving heat from a source is not necessarily the same as the change in the entropy of the source (unless it receives its heat reversibly, in which case the temperature of the substance is sensibly equal to that of the source throughout the process), it is quite possible to calculate this change in many cases. The first point to establish is that the entropy of a substance in any particular state depends only

on that state and not on the way it arrived there. To do this we must show that when a substance is taken round a complete cycle  $\int \frac{dH}{\theta} = 0$ . To begin with we will show how to take it round any reversible cycle.

It should be observed that to make the cycle reversible is only a question of adjusting the *external* conditions. Let the thick

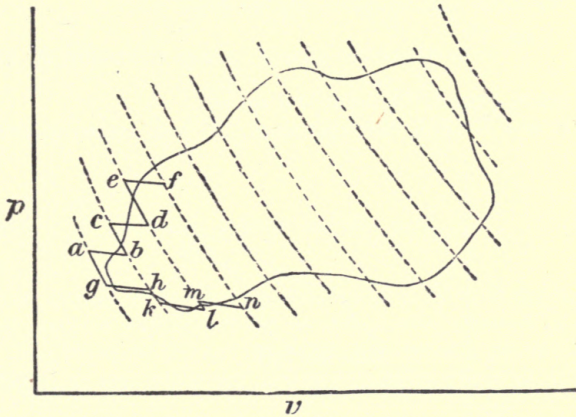


FIG. 136.

line represent any complete cycle. Draw a number of adiabatic curves represented by dotted lines, and let *ab*, *cd*, *ef* represent portions of isothermal curves corresponding to temperatures  $\theta_1$ ,  $\theta_3$ ,  $\theta_5$ , etc., and *gh*, *kl*, *mn* portions of isothermal curves corresponding to temperatures  $\theta_2$ ,  $\theta_4$ ,  $\theta_6$ , etc. If we are provided with a number of sources at  $\theta_1$ ,  $\theta_3$ ,  $\theta_5$ , etc., and sinks at  $\theta_2$ ,  $\theta_4$ ,  $\theta_6$ , etc., we can take the substance reversibly out along the zigzag path *abcdef* . . . and home by . . . *lkhga*.

If  $\delta H_1$ ,  $\delta H_3$ , etc., represent the heat absorbed along *ab*, *cd*, *ef*, etc., and  $\delta H_2$ ,  $\delta H_4$  the heat rejected along *hg*, *lk*, etc., then since *ab* and *hg* are the isothermals of the Carnot diagram *abl<sub>1</sub>g*

$$\frac{\delta H_1}{\theta_1} = \frac{\delta H_2}{\theta_2}$$

Similarly, since *cd* and *lk* are the isothermals of a Carnot diagram *cdlk*

$\frac{\delta H_3}{\theta_3} = \frac{\delta H_4}{\theta_4}$  and so on. Thus for the complete zigzag path we have

$$\frac{\delta H_1}{\theta_1} + \frac{\delta H_3}{\theta_3} + \frac{\delta H_5}{\theta_5} + \dots - \dots - \frac{\delta H_4}{\theta_4} - \frac{\delta H_2}{\theta_2} = 0 \quad (1)$$

By increasing the number of sources and sinks, and so taking the isothermals and adiabatics closer together, we can in the limit make the zigzag path practically coincide with the thick line, in which case we shall have taken the substance reversibly round the path and equation (1) becomes

$\left( \int \right) \frac{dH}{\theta} = 0$ , where the sign  $\int$  means the value of the integral taken round the complete cycle.

Let A and B (Fig. 137) represent any two states of the sub-

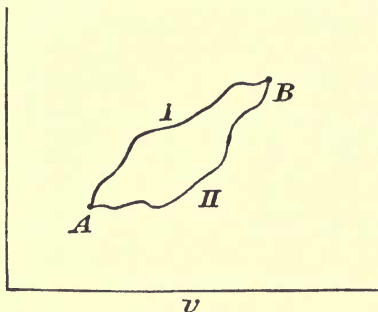


FIG. 137.

stance, and let I and II represent any two possible ways of getting the substance from state A to state B. It will be assumed that it is possible to adjust the external conditions so as to make either of these paths reversible; the value of  $\int \frac{dH}{\theta}$  for any portion is determined by the path.<sup>1</sup>

Taking the closed cycle from A up I and down II we have

$$\left( \int \right) \frac{dH}{\theta} = 0.$$

<sup>1</sup> It must be remembered that  $\theta$  is the temperature of the substance itself at any point. The amount of heat taken in and the temperature of the substance is fixed by the nature of the path. It is necessary to assume that the temperature of the substance is always uniform



Thus 
$$\left( \int_A^B \frac{dH}{\theta} \right)_I + \left( \int_B^A \frac{dH}{\theta} \right)_{II} = 0$$

But since the path II can be made reversible

$$\left( \int_B^A \frac{dH}{\theta} \right)_{II} = - \left( \int_A^B \frac{dH}{\theta} \right)_{II}$$

$$\therefore \left( \int_A^B \frac{dH}{\theta} \right)_I - \left( \int_A^B \frac{dH}{\theta} \right)_{II} = 0:$$

Thus  $\int_A^B \frac{dH}{\theta}$  does not depend on the path.

That is, change in entropy in passing from A to B depends only on the states A and B and not on the way in which B is reached

If then we knew the value of the entropy of a given mass of a substance at any state we can calculate its value at any other state provided we can evaluate the integral  $\int \frac{dH}{\theta}$  along any path from one state to the other. We do not, however, know the absolute value of the entropy corresponding to a substance in any particular state, but this does not matter very much in actual practice since we are usually concerned only with changes in entropy. In engineering work it is usual arbitrarily to fix some particular state as the starting point and call the entropy at that point 0. We can then give a value for the entropy at other states.<sup>1</sup>

Thus, in the case of steam, the starting point is taken as water at 0° C.; tables have been constructed showing the entropy of unit mass of steam at various temperatures and pressures.<sup>2</sup>

It will perhaps facilitate understanding if we work out the

<sup>1</sup> It should be observed that since we do not know the absolute value of the entropy we cannot compare the entropy of one substance with that of another.

<sup>2</sup> Callendar's *Abridged Steam Tables*—Edward Arnold & Co.

entropy of a pound of saturated steam at 100° C., leaving out certain corrections which rather complicate the issue.

Starting with water at 0°C. or 273° A., we can get to steam at 100° C. or 373° A. by any convenient route. Let us imagine we heat the water from 0° C. to 100° C. under sufficient pressure to prevent evaporation, and then let it evaporate at constant pressure of 760 mm. In heating the water we shall not make a serious error if we regard its specific heat as constant (cp. page 128, and equal to 1. To raise the temperature of 1 lb. of water through  $\delta T^\circ$  will therefore require  $1 \times \delta T$  or  $\delta T$  Thermal Units.

The change in entropy in passing from 273° A. to 373° A. will therefore be

$$\int_{273}^{373} \frac{dT}{T} = \log_e 373 - \log_e 273.$$

In order to evaporate the water at 100° C. or 373° A. under 760 mm. pressure we must supply it with the latent heat of evaporation at this temperature, which we may take as 539 T.U.

The gain in entropy during this operation will be

$$\frac{539}{373}$$

The entropy of the saturated steam will therefore be

$$\begin{aligned} & \log_e 373 - \log_e 273 + \frac{539}{373} \\ &= 2.3026(\log_{10} 373 - \log_{10} 273) + \frac{539}{373} \\ &= .3120 + 1.445 \\ &= 1.7570 \end{aligned}$$

The more accurately worked tables of Callendar give 1.7573. Entropy is usually denoted by the symbol  $\varphi$ .

**Applications of the Idea of Entropy.**—The change in entropy of a substance when passing from one state to another is, as we have stated, simply determined by the two states. The amount of heat taken in or rejected depends not only on the initial and final states, but also on the path by which the change takes place. It will be obvious that since the entropy change  $\varphi_2 - \varphi_1$  is defined

as  $\int \frac{dH}{\theta}$  the amount of heat absorbed or rejected will be smaller

the lower the average temperature during the change. If we know in some way the values of the entropy, and also the temperature at all parts, we can at once get the amount of heat absorbed. Take, for example, the case of the working substance of an engine taking in heat at a constant temperature  $\theta_1$ . If  $\varphi_1$  and  $\varphi_2$  are the initial and final values of the entropy of the substance, and the heat is taken in reversibly so that  $\theta_1$  represents the temperature of the substance as well as that of the source,

$$\text{Heat taken in} = \theta_1(\varphi_2 - \varphi_1).$$

In a practical case it is probable that the heat would not be taken in reversibly, for the temperature of the working substance at some parts of the path would fall below  $\theta_1$  (in fact it would have to do so if the heat passed into it at a finite rate), and so even though the substance started and finished at  $\theta_1$  the average temperature along the path would be somewhat less.

But as the substance finishes at the state where the entropy is

$\varphi_2$ , it follows that the heat taken in is  $\int_{\varphi_1}^{\varphi_2} \theta' d\varphi$  where  $\theta'$  represents

the temperature of the substance itself at each stage. In general we cannot find the various values of  $\theta'$ ; all we know is that on the average it is less than  $\theta_1$ .

Thus the heat taken in is less than  $\theta_1(\varphi_2 - \varphi_1)$ , where  $\theta_1$  is as before the temperature of the source supplying the heat.

We have in fact the general relation for the heat absorbed

$$\delta H = \theta \delta \varphi \text{ for reversible actions}$$

$$\delta H < \theta \delta \varphi \text{ for irreversible actions,}$$

where  $\theta$  in each case represents the *temperature at which the heat is supplied*; the second relation is brought about because the temperature of the substance in general differs by an unknown amount from that of the source.  $\delta \varphi$  in each case is the change in entropy of the substance.

**Temperature Entropy Diagrams.**—Much information as to the conditions in a heat engine can be obtained by means of a diagram of the changes in the working substance in which the co-ordinates are temperature and entropy; such diagrams are often referred to by engineers as  $\theta\varphi$  diagrams. We can illustrate this by drawing such a diagram for a Carnot cycle (Fig. 138).

Let the working substance take in heat at  $\theta_1$ . This isothermal

expansion is represented by AB. During the process the entropy of the substance increases from  $\varphi_1$  at A to  $\varphi_2$  at B. During an adiabatic change  $\delta H = 0$ , and so  $\int \frac{dH}{\theta} = 0$ , so that an adiabatic represents a line of constant entropy or an "isentropic."

Let BC represent the adiabatic expansion. CD represents the isothermal compression, during which the entropy changes back from  $\varphi_2$  to  $\varphi_1$ . The substance then returns to A by the adiabatic DA, during which there is no change in entropy. The heat taken in along AB is  $\theta_1(\varphi_2 - \varphi_1)$ , and that rejected along CD is  $\theta_2(\varphi_2 - \varphi_1)$

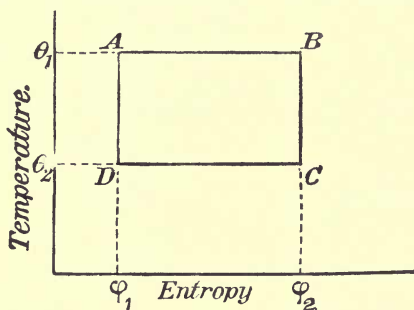


FIG. 138.

The amount converted into work is therefore  $(\theta_1 - \theta_2)(\varphi_2 - \varphi_1)$ , that is to say the area of the diagram ABCD.

In actual engines the cycles in use differ from a Carnot cycle in various ways owing to practical considerations ; if we can draw the  $\theta\varphi$  diagram for the cycle, the area of the diagram will represent the heat which is converted to work. This statement is not of course a fresh law ; it follows from the definition of entropy

$$\text{as } \int \frac{dH}{\theta}.$$

Such cycles usually have some portion which is irreversible : nevertheless we can still determine the conditions of the path in some cases and so draw an entropy temperature diagram in which the temperatures really represent the temperature of the substance, so that  $\delta H = \theta\delta\varphi$ .

If however there occur also fortuitous irreversible changes, e.g. conduction to the cylinder walls, the temperature of the working

substance will differ by an indeterminate amount from that which is credited to it on the diagram. These fortuitous changes mean that less heat is converted to work than the area of the  $\theta\phi$  diagram.<sup>1</sup>

Thus the  $\theta\phi$  diagram tells us the amount of heat which ought to be converted to work and enables us to decide how far one cycle is better than another apart from fortuitous losses. The indicator diagram shows how much work is being done on the piston, and so we can see whether these fortuitous losses are occurring.

It may not be out of place to emphasize the fact that all this conception of entropy is merely a way of expressing in a more easily visualized form the consequences of the Second Law of Thermodynamics.

It has been developed very much further than is here indicated, and a large number of equations formed which represent the possible behaviour of systems under a variety of conditions. One such equation is a good deal used in Chemistry under the title of the Phase Rule. All these equations are merely developments of the First and Second Laws of Thermodynamics; their treatment is more suited to a larger work than the present.

<sup>1</sup>  $\delta H \leq \theta \delta \phi$ , but is not greater. This comes in in two ways.  $\delta H$  is the heat *absorbed*, so that heat rejected is negative. Thus if  $-\delta H < -\theta \delta \phi$  the heat rejected is numerically *greater* than  $\theta \times$  decrease in entropy. Thus less heat is absorbed and more rejected. It is easily seen that if the working substance is giving out heat to a sink it is likely to be at a higher temperature than the sink.



# QUESTIONS

## PART I

### CHAPTER II

1. Describe a method of filling and sealing a thermometer.
2. Why is the bulb of a thermometer usually made cylindrical ?
3. Explain what is meant by the "fixed points" on a thermometer. Describe how you would determine them for a given instrument, pointing out the reasons for any precautions you would take.
4. In using a hypsometer to determine the upper fixed point of a thermometer, why is it necessary to have a manometer and also to read the barometer ?
5. What do you understand by a scale of temperature ?
6. Express the following temperatures on the Centigrade scale:  $98.4^{\circ}$  F.,  $350^{\circ}$  F.,  $10^{\circ}$  F.,  $-10^{\circ}$  F.,  $20^{\circ}$  R.
7. Express the following temperatures on the Fahrenheit scale:  $15^{\circ}$  C.,  $-15^{\circ}$  C.,  $-273^{\circ}$  C.,  $10^{\circ}$  R.
8. Describe the general arrangement of a mercury thermometer suitable for temperatures up to  $400^{\circ}$  C.
9. Describe some form of maximum and minimum thermometer.
10. Explain as clearly as you can what is meant by the temperature of a body : in the course of your answer distinguish between temperature and heat, and point out the fundamental test which decides whether two bodies are, or are not, at the same temperature.
11. Explain how a thermometer is graduated, what is the precise meaning of  $50^{\circ}$  C. on the mercury-in-glass scale ?

### CHAPTER III

1. What is meant by the coefficient of linear expansion of a substance ?

The iron tubular bridge over the Menai Straits is rather more than 1,500 feet long. What would be its increase in length for a change of temperature from  $0^{\circ}$  C. to  $18^{\circ}$  C. ? (Coefficient of linear expansion of iron =  $.000012$ .)

2. A brass metre scale is correct at  $0^{\circ}$  C. : what would be its length at  $20^{\circ}$  C. (Coefficient of linear expansion of brass =  $.000019$ .)

3. The distance between two points was measured by means of the above scale and appeared to be 40.5 cm. If the temperature was  $15^{\circ}$  C., what was the true distance between the points ?

4. A steel measuring tape, 66 feet long, is correct at 60° F. : how much would it contract if cooled to 32° F. ? (Coefficient of linear expansion of steel =  $\cdot 000011$  per degree Centigrade.)

5. Certain types of vernier callipers are made reading to  $1/50$  mm. ; they are constructed of steel. If such an instrument were used to measure objects up to 10 cm. long in a laboratory where the temperature might vary through a range 20° C., would it be worth while correcting the reading for temperature ?

6. Describe a method of determining the coefficient of linear expansion of a metal such as copper or iron.

7. Describe an accurate method of determining the coefficient of linear expansion of a solid ; and discuss the degree of accuracy to which the method may be trusted.

8. A cylindrical bar of iron,  $\frac{1}{2}$  inch in diameter, just fits at 15° C. with its ends in contact with two fixed stops. If the bar is heated to 200° C. and the stops cannot yield, what is the force exerted on them ? (Coefficient of linear expansion of iron =  $\cdot 000012$  ; Young's modulus, compression or tension, = 12,500 tons per sq. inch.)

9. During a demonstration of rapid fire at Hythe with a rifle (S.M.L.E.) in which forty-two rounds were fired in a minute, it was noted that at the start the end of the barrel was flush with the nose-cap, and at the end it was projecting quite  $\frac{1}{8}$  inch. Calculate the average temperature of the barrel (assuming it started at 10° C.). Initial length of barrel about 2 feet 1 inch ; coefficient of linear expansion of steel =  $\cdot 000011$ .

10. The diameter of a brass cylinder, as measured by a pair of steel callipers, is 3.25 cm. when the temperature is 22° C. Find (a) its true diameter at 22° C., (b) its diameter at 0° C. The callipers are correct at 0° C.

## CHAPTER IV

1. In practical life, the thermal expansion of solids can sometimes be made to serve a useful purpose, while in other cases it is a nuisance which has to be overcome by some compensating device. Give an example of each case.

2. Explain clearly why any attempt to boil water in a thick glass vessel is almost certain to crack the vessel, while in the case of thin glass the operation can be carried out quite safely. Illustrate your answer by considering the behaviour of vessels made of fused silica.

3. What is the object of annealing glass vessels and glass joints after they are made ? Describe any experiment which illustrates the necessity of this process.

4. Describe and explain the action of any form of thermostat.

5. Describe the construction and working (a) of a compensated balance wheel, (b) some form of compensated pendulum.

6. When it is necessary to seal a wire through glass, platinum is generally used. Why is this ?

7. Nickel steel alloys have certain important properties. What is the special practical importance (*a*) of the alloy with 36 per cent. of nickel, (*b*) that with 45 per cent. of nickel ?

8. Describe the construction of an invar pendulum. Why are balance wheels of watches not made of invar ?

## CHAPTER V

1. Distinguish between absolute and apparent expansion of a liquid. How would you determine the coefficient of apparent expansion of a liquid such as mercury ?

2. A glass pycnometer containing 250 gm. of mercury at  $0^{\circ}$  C. is heated to  $100^{\circ}$  C., and when reweighed is found to contain 246.09 gm. Calculate the coefficient of apparent expansion of mercury.

3. A specific-gravity flask when empty weighs 13.45 gm. It is filled with alcohol at  $15^{\circ}$  C. and found to weigh 72.36 gm. It is then placed in a water-bath and maintained at  $50^{\circ}$  C. for some time. When reweighed the flask and its contents are found to weigh 70.27 gm. Calculate the coefficient of apparent expansion of alcohol.

4. In experiments with pycnometers or weight thermometers the value of the coefficient is worked out by comparing the weight of liquid expelled with that of the liquid remaining in the vessel. Explain why this is so, and point out the error which would arise if the weight of liquid originally in the vessel were taken instead of the weight of liquid finally left in.

5. The coefficient of absolute expansion of mercury has been determined with great care, and the results can be used to standardize glass pycnometers. Calculate the coefficient of cubical expansion of the pycnometer in Question 2, taking the coefficient of absolute expansion of mercury between  $0^{\circ}$  and  $100^{\circ}$  C. as .0001825.

6. What is the relation between the coefficient of linear expansion of a solid and its coefficient of cubical expansion ? If the coefficient of linear expansion of fused silica is .0000005, what is the coefficient of cubical expansion of a vessel made of fused silica ?

7. For nearly all purposes, the coefficient of expansion of a liquid, as determined by means of a fused silica pycnometer, may be regarded as the absolute expansion of the liquid. Illustrate the truth of this statement by considering the error introduced by neglecting the expansion of the silica in the case of (*a*) mercury, (*b*) glycerine, of which the coefficients of absolute expansion are respectively .0001825 and .00053.

8. Describe with the aid of a graph the changes in volume which take place when water is gradually heated from  $0^{\circ}$  C. to about  $15^{\circ}$  C. How would you illustrate these changes experimentally ?

9. Explain clearly how a knowledge of the ratio of the densities of a liquid at two different temperatures enables the coefficient of expansion to be calculated.

10. A glass bulb (loaded with shot inside) is weighed in air, and found to weigh 49.360 gm. It is then suspended in alcohol so as to be completely immersed. When the alcohol is at  $15^{\circ}\text{C}$ . the apparent weight of the bulb is 10.237 gm.; with the alcohol at  $30^{\circ}\text{C}$ . the apparent weight is 10.860 gm.

Calculate the coefficient of apparent expansion of alcohol.

11. Describe a method by which the coefficient of absolute expansion of mercury has been determined. In your description explain how it is that the expansion of the tube does not come into the result.

12. Regnault's apparatus for determining the expansion of mercury was a great improvement on that of Dulong and Petit. What are the chief points in which the improvement consists?

13. In an experiment made with Dulong and Petit's apparatus to determine the expansion of mercury, the column at  $0^{\circ}\text{C}$ . was 65.2 cm. high and the column at  $100^{\circ}\text{C}$ . was 1.18 cm. higher. Calculate the coefficient of absolute expansion of mercury.

14. In the experiment to Question 13, to what degree of accuracy should the difference in height of the two columns be measured in order that the uncertainty in this measurement may not produce a greater probable error in the result than would be produced by measuring the coefficient with a silica pycnometer and neglecting the expansion of the vessel? (For expansion of silica, see Question 6.)

15. The pressure of the atmosphere is found from a barometer reading. The height of column of mercury is read off on a brass scale (correct at  $0^{\circ}\text{C}$ .) and found to be 75.51 cm., the temperature being  $16^{\circ}\text{C}$ .

Calculate the true pressure, expressed as a column of mercury at  $0^{\circ}\text{C}$ .

(Coefficient of linear expansion of brass, .000019; coefficient of absolute expansion of mercury, .000182.)

## CHAPTER VI

1. State Boyle's Law, and describe an experiment by which it may be verified.

2. Gases such as hydrogen and oxygen are often stored under pressure in steel cylinders; the usual pressure in such cylinders when "full" is 120 atmospheres. What would be the capacity of a cylinder intended to hold 20 cubic feet of oxygen (measured at atmospheric pressure)?

3. On fitting a pressure gauge to a 10-cubic-foot oxygen cylinder (which had already been used) the pressure was found to be 80 atmospheres. How much oxygen was there still available?

4. In filling a barometer tube, a certain amount of air was accidentally admitted. It was found that when a standard barometer read 76.5 cm. the faulty barometer stood at 75.4 cm. and the surface

of the mercury was 5.8 cm. from the closed end of the tube. On a later occasion the faulty barometer read 74.5 cm. : what would have been the reading of a correct one ?

5. If the temperature of a given quantity of gas changes and the pressure is kept constant, what is the relation between the volume of the gas and its temperature ?

Describe an experiment for determining the coefficient of expansion, at constant pressure, of a gas such as air.

6. Describe a method of determining the pressure coefficient for a gas at constant volume.

Why would you expect the pressure coefficient of a gas to be equal to the volume coefficient ?

7. The pressure of the air in the tyres of a car was 75 lb. per square inch when the temperature was  $15^{\circ}\text{C}$ . Later on the car stood in the sunshine and the temperature went up to  $25^{\circ}\text{C}$ . Calculate the pressure of the air in the tyres, assuming that the latter did not expand.

8. In a determination of the pressure coefficient with an apparatus of the type of Fig. 37, it was found that with the bulb in melting ice the gas was brought to its fixed volume when the level of the mercury in the open limb was 3.2 cm. below that in the other. With the bulb in steam, the mercury in the open limb had to be 23.2 cm. above the other. The barometer reading was 75.5 cm. Calculate the pressure coefficient. (Temperature of steam at 75.5 cm. pressure =  $99.8^{\circ}\text{C}$ .)

9. Describe a form of gas thermometer.

Gas thermometers are usually of the constant-volume type. Can you suggest any reason for this ?

10. Gas thermometers have certain great advantages, but also have disadvantages which make them unsuitable for use on many occasions. Mention some of the chief advantages and disadvantages. What is the principal use of a gas thermometer ?

11. For a certain constant-volume hydrogen thermometer, the pressure necessary to bring the gas to its fixed volume when the bulb was in melting ice was 1,000 mm. of mercury : with the bulb in steam (at standard pressure) the pressure required was 1,365 mm. In the course of a test of a mercury thermometer, the latter was placed alongside the bulb of the gas thermometer in a water-bath : the pressure required to bring the hydrogen to its fixed volume was 1,212 mm., while the mercury thermometer read  $60^{\circ}\text{C}$ . What was the true temperature of the bath (as given by the hydrogen thermometer) ?

12. What is meant by the absolute scale of temperature ?

Explain how the use of this scale simplifies calculations of the volumes of gases at different temperatures.

13. What is meant by the absolute zero of temperature ?

What is its value (a) on the Centigrade scale, (b) on the Fahrenheit scale ?

14. A certain quantity of gas was formed to occupy a volume of 450 c.c. when its temperature was  $16^{\circ}\text{C}$ . and its pressure 75 cm. of mercury. What volume would it occupy at  $0^{\circ}\text{C}$ . and 76 cm. of mercury ?



15. A cubic foot of hydrogen, measured at  $0^{\circ}\text{C}$ . and 760 mm. of mercury, weighs .0056 lb. What would be the weight of a cubic foot of hydrogen measured at  $15^{\circ}$  and 760 mm. ?

16. In calculations on the buoyancy of airships it is necessary to know the density of the air at different elevations. If a cubic metre of air at ground level, when the temperature is  $9^{\circ}\text{C}$ . and the pressure 1,014 millibars, weighs 1,253 gm., what would be the weight of a cubic metre of air at 3,300 feet if the temperature at this elevation is  $5^{\circ}\text{C}$ . and the pressure 900 millibars ?

## CHAPTER VII

1. How is quantity of heat defined, and what is meant by a unit of heat ?

What is meant by the statement that the calorific value of a certain gas is 450 B.Th.U. per cubic foot ?

2. Gas companies base their charges for gas entirely on the total amount of heat which could be obtained from the gas supplied. A certain company charged  $14\frac{1}{2}$  pence per therm (1 therm = 100,000 B.Th.U.). What would be the cost of heating the water for a bath by means of a geyser, if the water entered the geyser at  $60^{\circ}\text{F}$ . and came out at  $110^{\circ}\text{F}$ ., the amount of water used being 24 gallons, i.e. 240 lb. ? Assume that the whole of the heat from the gas went into the water.

3. What is meant by the thermal capacity of a body ? Two hundred gm. of water, at  $30^{\circ}\text{C}$ ., are poured into a metal vessel originally at  $15^{\circ}\text{C}$ ., the temperature of the room. The water is stirred and its temperature is found to have dropped to  $28.5^{\circ}\text{C}$ . Calculate the amount of heat communicated to the vessel and from this its thermal capacity.

4. Describe in detail any method by which the heat of combustion of coal may be determined.

5. In a determination of the heating value of coal by means of a Darling calorimeter the following figures were obtained :—

Weight of coal burnt . . . . .	1.52 gm.
Initial temperature of the water in the calorimeter . . . . .	$13.20^{\circ}\text{C}$ .
Highest temperature of water . . . . .	$20.65^{\circ}\text{C}$ .
Mass of water in calorimeter . . . . .	1,400 gm.
Water equivalent of apparatus . . . . .	210 gm.

Calculate the heating value of coal from these figures.

6. What is meant by the specific heat of a substance ? Is it necessary to specify the units of mass or the scale of temperature in giving the value of the specific heat ?

Describe a method of determining the specific heat of a metal like iron or tin.

7. A lump of lead weighing 752 gm. was heated to  $100^{\circ}\text{C}$ . and then immersed in 500 gm. of water contained in a copper calorimeter. The initial temperature of the water was  $15.0^{\circ}\text{C}$ . ; the final temperature of the water was  $18.6^{\circ}\text{C}$ . The empty calorimeter weighed 200 gm.,

and the specific heat of copper is  $\cdot 095$ . Calculate the specific heat of lead.

8. In the experiment described in Question 7, the weighings were made to the nearest gm., but the temperature of the water was measured by means of a good thermometer reading to tenths of a degree. Explain why it was necessary to measure the temperature to such a degree of accuracy.

9. In order to determine the specific heat of aniline, a lump of copper, weighing 320 gm., was heated to  $100^{\circ}\text{C}$ . and then immersed in 468 gm. of aniline contained in a copper calorimeter of which the weight was 200 gm. The initial temperature of the aniline was  $10^{\circ}\text{C}$ . and the final  $19\cdot 5^{\circ}\text{C}$ . Calculate the specific heat of aniline, taking that of copper as  $\cdot 095$ .

10. In order to obtain an approximate value for the temperature of a furnace, a piece of iron weighing 1 lb. was left in the furnace for some time and then quickly withdrawn and plunged into  $6\frac{3}{4}$  lb. of water contained in a calorimeter of which the water equivalent was  $\frac{1}{4}$  lb. The original temperature of the water was  $13^{\circ}\text{C}$ ., and the final temperature (after adequate stirring) was  $38^{\circ}\text{C}$ . Calculate the temperature of the furnace, taking the mean specific heat of iron over the expected range as  $\cdot 15$ .

11. Describe how you would determine the specific heat of a liquid by the method of cooling.

12. In a determination of the specific heat of a liquid a quantity of the liquid was heated and placed in a metal vessel provided with an adequate stirrer. The water equivalent of the vessel was 8 gm., and the mass of liquid 154 gm.

The rate of cooling was as follows:—

$50^{\circ}\text{C}.$ – $45^{\circ}\text{C}$ .	required	167	seconds.
$45^{\circ}\text{C}.$ – $40^{\circ}\text{C}$ .	„	190	„
$40^{\circ}\text{C}.$ – $35^{\circ}\text{C}$ .	„	230	„

Repeating the experiment with an equal volume of water (mass = 150 gm.) in the vessel, the times were:—

$50^{\circ}\text{C}.$ – $45^{\circ}\text{C}$ .	required	300	seconds.
$45^{\circ}\text{C}.$ – $40^{\circ}\text{C}$ .	„	350	„
$40^{\circ}\text{C}.$ – $35^{\circ}\text{C}$ .	„	405	„

Calculate the specific heat of the liquid.

## CHAPTER VIII

1. What is meant by the term heat engine ?

In the working of heat engines there are certain broad principles common to all types. What are these principles ?

2. What is meant by (a) work, (b) power ?

What is meant by the brake-horse-power of an engine and how may it be measured ?

3. In a test of a certain engine, a rope brake was used. A load of 80 lb. weight was attached to one end of the rope and a spring balance

to the other. The diameter of the wheel (measured to the centre of the rope) was 4 feet, and with the engine running at 410 revolutions per minute the reading of the spring balance was 16 lb. weight. Calculate the B.H.P. developed by the engine.

4. Describe the arrangement and working of a double-acting steam-engine cylinder. Show how this action is an example of the general processes characteristic of all heat engines.

5. Describe the action of an internal-combustion engine, working on the four-stroke cycle.

6. What connection is there between heat and mechanical work? What is meant by the mechanical equivalent of heat?

7. Describe a laboratory method of determining the mechanical equivalent of heat and mention any precautions and corrections which are necessary.

8. In an experiment to determine the mechanical equivalent of heat, a brass drum containing 250 gm. of water was driven against the friction of a silk belt, and the temperature was noted every minute. At the end of eight minutes the drum was stopped, the ends of the belt detached from their loads and fastened together, and the motor started again; the rate of cooling was noted. The following figures were obtained:—

Room temperature . . . . .	15° C.
Diameter of drum . . . . .	6 inches.
Water equivalent of drum . . . . .	39 gm.
Load on one end of belt . . . . .	4,275 gm.
Load on other end of belt . . . . .	(473—spring balance reading)

## WORKING

## COOLING

Time (Minutes).	Temperature.	Revolution Counter.	Spring Balance (lb.).
0	14.0° C.	5,184	.50
1	16.0	5,313	.50
2	17.9	5,441	.50
3	19.8	5,576	.50
4	21.6	5,713	.50
5	23.2	5,845	.45
6	24.8	5,979	.45
7	26.3	6,116	.45
8	27.8	6,249	—

Time (Minutes).	Temperature.
8½	27.8° C.
9	27.4
10	26.8
11	26.2
12	25.6
13	25.1
14	24.6
15	24.1
16	23.7

Determine the total amount of heat supplied to the drum and its contents, making the necessary correction for cooling.

Determine also the work done against friction, and hence calculate the mechanical equivalent of heat. (1 lb. = 454 gm.)

9. The heat of combustion of a pint of petrol is about 9,600 T.U. A certain engine was found to use 3 pints of petrol per hour when it was developing 4 B.H.P. What fraction of the heat supplied was converted to useful work? (Mechanical equivalent of heat = 1,400 foot-pounds per T.U.)

10. A certain car is found to run on the average 30 miles to each gallon of petrol used. Assuming that the engine converts  $\frac{1}{3}$  of the heat supplied into useful work, calculate the work done in driving the car 30 miles, and hence the average resistance which has to be overcome when the car is moving.

11. In a very efficient steam engine, the consumption of coal per B.H.P. was 1.25 lb. per hour. The coal had a heating value of 15,000 B.Th.U. per lb. Calculate the brake thermal efficiency of the engine. ( $J = 778$  foot-pounds per B.Th.U.)

12. The thermal efficiency of all practical heat engines is very low. Why is this? Is there any likelihood of improvement in design producing efficiencies anywhere near 100 per cent.? Give reasons for your answer.

13. In determining the power of large engines the ordinary friction brake cannot be used, and some other method (e.g. measurement of shaft torsion) is adopted. Explain why this is so and illustrate your answer by considering the heat which would be developed in the case of a 10,000 H.P. engine.

14. The Mark VII bullet leaves the rifle with a speed of 2,440 feet per second. The ordinary expressions of mechanics show that in the absence of any air resistance a body projected vertically with this velocity would rise to a height of about 93,000 feet. If the bullet weighs  $\frac{1}{2}$  ounce, how much work does it do in the ascent?

If the bullet were fired directly into a sandbank and the whole energy converted to heat, what quantity of heat would be generated?

15. What do you understand by the Principle of the Conservation of Energy?

Illustrate your answer by working the following example: Experiment shows that when a rifle is fired vertically, using Mark VII ammunition, the air friction is such that the bullet rises not quite 10,000 feet. When it falls again it reaches the ground with a velocity of about 500 feet per second, i.e. the velocity it would acquire by falling about 3,900 feet in the absence of air resistance.

Calculate the amount of heat which is generated (a) on the upward journey, (b) on the downward? How does the total amount compare with that in Question 14?

16. Give an account of the experimental work which led to the idea of the equivalence of heat and mechanical energy.

17. In scientific and engineering discussions, various units are employed to measure work and energy, e.g. the foot-pound, the erg ( $= 1$  centimetre-dyne), the joule ( $= 10^7$  ergs), the kilogram-metre. If the value of  $J$  is given as 778 foot-pounds per B.Th.U., calculate its value—

(a) in foot-pounds per T.U.;

(b) in ergs per calorie;

(c) in kilogram-metres per large (kilogram) calorie.

(2.54 cm. = 1 inch.  $g$  may be taken as 981 cm. per sec. per sec., so that a force of 1 gm. weight represents 981 dynes.)

18. Mention the chief general methods which have been used in the determination of  $J$ , and describe one method in greater detail.



19. Describe a "continuous-flow" method of determining  $J$ , such as that of Reynolds and Moorby, or Callendar and Barnes. Mention any advantages of using a continuous flow.

20. Electrical power is usually measured in watts (1 watt =  $10^7$  ergs per second). An electric kettle holds  $1\frac{1}{2}$  pints of water and is stated to take 350 watts. How long should it take to raise the temperature of the water from  $15^\circ\text{C}$ . to  $100^\circ\text{C}$ . if 80 per cent. of the heat is utilized? (Take the water equiv. of the kettle as  $\frac{1}{4}$  lb.; 1 pint of water weighs  $1\frac{1}{4}$  lb.;  $J = 4.2 \times 10^7$  ergs per calorie, 454 gm. = 1 lb.)

21. In accurate scientific work it is necessary in defining a unit of heat to specify the particular range of temperature, e.g. the 15-degree calorie.

Mention any experimental work which shows that this precaution is necessary.

## CHAPTER IX

1. Comment on the following, and describe any experiment to illustrate the cause of the phenomena:

(a) Ice floats on water.

(b) After a very cold night the water-pipes of a house are sometimes found to have burst.

(c) The action of frost in breaking up soil and rocks.

2. A lump of cast iron will float in the molten liquid, but in the case of most metals, e.g. copper, the solid sinks in the liquid. Explain clearly why it is possible to obtain sharp castings with iron but not with a metal like copper.

3. A piece of ice at  $-5^\circ\text{C}$ . is gradually heated. Illustrate, with the aid of a graph, how the volume changes as the temperature rises from  $-5^\circ\text{C}$ . to  $15^\circ\text{C}$ .

4. Large masses of snow often remain quite a long time after a thaw has set in, especially if they are not exposed to wind; e.g. snow is usually to be found in the gullies of the north face of Great End (Lake District), even in May. Why is this?

5. What is meant by the latent heat of fusion of a substance?

What quantity of heat would be required just to melt 2 kilograms of lead originally at  $15^\circ\text{C}$ .?

(Specific heat of lead = .031, melting-point  $327^\circ\text{C}$ . Latent heat of fusion, 5 calories per gramme.)

6. A calorimeter (water equivalent 20 gm.) contains 500 gm. of water at  $20^\circ\text{C}$ .

What weight of dry ice originally at  $0^\circ\text{C}$ . must be added to the water in order that the temperatures may be reduced to  $10^\circ\text{C}$ .?

What would be the result of adding 160 gm. of ice? (Latent heat of fusion of ice = 80 calories per gm.)

7. What is meant by the melting-point of a solid? Illustrate your answer by describing what happens when a solid is gradually heated from a temperature well below the melting-point to one well above it, taking as examples ice and paraffin wax.



8. Describe in detail a method of determining the melting point of a solid.

9. Skating becomes very difficult if the temperature is greatly below freezing-point—the skate will not “bite.” Explain why this is so, and describe an experiment to illustrate your answer.

10. It is usual to define  $0^{\circ}\text{C}$ . as the temperature at which pure ice melts rather than the temperature at which pure water freezes. Can you suggest any reason for this?

11. In what way is the melting-point of a solid affected by pressure? Illustrate your answer by reference to the following points:

(a) When one is walking on snow a hard mass more or less of ice is apt to be formed under the heel of one's boot, but it does not do so if the temperature is very low.

(b) The temperature at points in the earth far below the surface must be above the melting-point of any known substance, but there is every reason to believe that the interior of the earth is not liquid.

(c) In determining the lower fixed point of a thermometer, great care is taken to have the ice pure, but no correction for the barometer reading is required (as far as the temperature is concerned)

12. Describe the behaviour of a mixture of ice and salt. In the course of your answer deal with the following point:

To make a very fair freezing mixture salt can be added to ice; a good way of melting ice on a frozen doorstep is to add salt to it.

13. Small pieces of ice at  $-10^{\circ}\text{C}$ . were added (with constant stirring) to 200 gm. of water contained in a calorimeter of water equiv. 10 gm. The original temperature of the water was  $18^{\circ}\text{C}$ ., and when it had dropped to  $8^{\circ}\text{C}$ . the whole was weighed and it was found that 22.6 gm. of ice had been added. Calculate the specific heat of ice, taking the latent heat of fusion as 80 calories per gm. Would you regard this as an accurate method of finding the specific heat? Give reasons for your answer.

## CHAPTER X

1. What do you understand by the boiling-point of a liquid? Illustrate your answer by describing what happens when a flask containing some water, and fitted with a thermometer and outlet tube, is heated over a burner.

2. Describe experiments which illustrate how the boiling-point of a liquid depends on the pressure to which it is exposed.

3. What is meant by the latent heat of vaporization of a liquid?

Describe a method of determining the latent heat of vaporization of water at  $100^{\circ}\text{C}$ .

4. Twenty gm. of steam at  $100^{\circ}\text{C}$ . are passed into 500 gm. of water at  $15^{\circ}\text{C}$ . contained in a calorimeter of water equivalent 20 gm. Calculate the final temperature of the water. (Latent heat of vaporization of water at  $100^{\circ}\text{C}$ . = 539 calories per gm.)

5. A certain boiler worked at a pressure of 160 lb. per sq. inch.

At this pressure water boils at  $188^{\circ}\text{C}$ . If the feed-water entered the boiler at a temperature of  $90^{\circ}\text{C}$ ., it was found that 11 lb. of steam were produced for each pound of coal burnt. Taking the latent heat of vaporization of water at  $188^{\circ}\text{C}$ . as 477 T.U. per lb. and the heating value of the coal as 8,400 T.U. per lb., calculate what percentage of the heat supplied has gone into the steam.

6. Exhaust steam from an engine passes into a surface condenser, i.e. a vessel in which are a number of tubes through which cooling water circulates: the steam is condensed by contact with the outside of these pipes, but does not mix with the cooling water. The pressure in the condenser is 4 lb. per square inch absolute, at which pressure the temperature of the steam is  $67^{\circ}\text{C}$ . and the latent heat of vaporization is 558 T.U. per lb. A steady state is reached in which the cooling water enters the pipes at  $15^{\circ}\text{C}$ ., and leaves at  $30^{\circ}\text{C}$ ., while the water from the condensed steam (which is pumped out) is at  $50^{\circ}\text{C}$ . Calculate the amount of heat which has to be abstracted from each pound of steam to condense it to water at  $50^{\circ}\text{C}$ ., and hence the number of pounds of cooling water required per pound of steam.

7. Observations of the boiling-point of water on the summit of a mountain enable the height of the mountain to be deduced. Explain why this is so and describe a suitable apparatus for making the observation.

8. What is meant by evaporation ?

Illustrate your answer by considering what happens when an open vessel containing some liquid is placed in a large enclosure.

9. What is meant by the saturated vapour pressure of a liquid ? Describe a method of determining the vapour pressure of water at different temperatures between say  $15^{\circ}\text{C}$ . and  $100^{\circ}\text{C}$ .

10. What is meant by ebullition or boiling ?

What is the characteristic feature which distinguishes boiling from ordinary evaporation ?

Why cannot a liquid boil until its temperature is such that the vapour pressure is equal to the pressure to which the liquid is exposed ?

11. How would you determine the boiling-point of a liquid of which only a small quantity is available ?

12. How can the vapour pressure of liquids at high temperatures be determined ?

13. A dish of water is placed in an enclosure. Compare (a) the rate of evaporation, (b) the final pressure of water vapour in the enclosure in the three following cases: (1) when the enclosure at the beginning is vacuous, (2) the enclosure originally contains dry air, (3) the enclosure contains air with a certain amount of water vapour already in it.

14. Why do puddles of water on a road dry up more quickly when a wind is blowing than they do in still air ?

15. One is almost certain to catch a chill if one sits about in wet clothes, especially if there is a draught; on the other hand, it is quite safe (but rather uncomfortable) to get straight out of a cold bath and dress without drying. Explain why this is so.

16. Large masses of snow are often seen to diminish perceptibly

in size after being exposed for some time to the action of wind, even though the temperature all the time is below freezing-point.

Explain why this is so.

17. What is meant by an unsaturated vapour? Is there any real distinction between the physical properties of unsaturated water vapour and a gas like sulphur dioxide at ordinary temperatures?

18. At one time, gases like oxygen and hydrogen were referred to as "permanent gases" to distinguish them from gases like sulphur dioxide and chlorine, which could be liquefied by pressure. Is there any real difference between the so-called permanent gases and the others, and if there is any difference, in what does it consist?

19. If a stream of air is blown through ether in an open flask, a very marked cooling effect is noted. Explain clearly why this is so. A similar process with water instead of ether produces a much smaller cooling effect, although the latent heat of vaporization of water is greater than that of ether. Why is this?

20. Describe and explain the general principles on which an ammonia refrigerating machine works.

21. Describe the construction of Bunsen's ice calorimeter and explain how it can be used to measure accurately the specific heat of a metal. What are the special advantages of a calorimeter of this type?

22. Describe a form of Joly's steam calorimeter, and mention any advantages of the apparatus.

A piece of aluminium, weighing 12.32 gm., was placed in the chamber of a steam calorimeter. The initial temperature of the aluminium was 15° C. Steam was then passed in, and when a steady state was reached it was found that the weight of steam condensed (after allowing for buoyancy) was .408 gm. Taking the latent heat of vaporization of water as 539 calories per gm., calculate the specific heat of aluminium.

23. Describe a method of determining the specific heat of a solid at very low temperatures.

## CHAPTER XI

TABLE OF SATURATED VAPOUR PRESSURE OF WATER

Temperature. °C.	2°.	4°.	6°.	8°.	10°.	12°.	14°.	16°.	18°.	20°.
Vapour pressure, mm. of mer- cury . . .	5.3	6.1	7.0	8.0	9.2	10.5	12.0	13.6	15.5	17.5

1. If a vessel containing a cool liquid (e.g. a tankard of beer from a cool cellar) be brought into a warm room, the outside of the vessel becomes moist although no liquid has been spilled. Explain how this happens.

2. What is meant by the relative humidity of the air? On a hot day in summer the air feels dry, but the amount of water vapour in a given volume of it (as determined by passing it through a weighed "drying" tube) may be greater than that in the same volume of air on a damp, cold day. Why is this?

3. Explain how a deposit of dew is formed. Why is dew much more likely to form when the air is still than when a wind is blowing? Why does it form more readily on objects near the ground than on those which are at a higher elevation?

4. A clear still night, following a hot, dry day, is a condition very favourable to the formation of dew. Why is this such a favourable condition?

5. Describe either Dine's or Regnault's hygrometer; explain how you would use it to determine the dew-point, and point out any precautions which are necessary.

6. Explain clearly how to calculate the relative humidity of the air when the dew-point has been determined.

7. On a certain day the temperature of the air is  $16^{\circ}\text{C}$ . and the dew-point is  $8^{\circ}\text{C}$ .

Calculate the relative humidity of the air.

8. On a certain day, the temperature is  $18^{\circ}\text{C}$ . and the relative humidity is 50 per cent.; on another day the temperature is  $6^{\circ}\text{C}$ . and the relative humidity 90 per cent. Which day would feel to be the drier, and on which day would the amount of water per unit volume be the greater?

9. Describe the wet-and-dry bulb hygrometer and explain how it works. Why is this instrument used in meteorological stations rather than one of the dew-point type such as Dine's?

10. Describe how the wet-and-dry bulb thermometer is modified in modern work so as to make it less uncertain.

11. What is the principle of Crova's dew-point hygrometer? Why is this a great improvement on earlier dew-point instruments?

12. A quantity of gas is collected over water, the temperature being  $14^{\circ}\text{C}$ . and the pressure to which it is exposed being 758 mm. of mercury. What would be the pressure of the gas if all the water vapour were removed from it and it occupied the same volume as it did when wet?

13. On dissolving a piece of metal in acid, hydrogen was given off; it was collected over water and the volume found to be 500 c.c. The temperature was  $14^{\circ}\text{C}$ . and the pressure 765 mm. of mercury.

If one litre of dry hydrogen at  $0^{\circ}\text{C}$ . and 760 mm. weighs .09 gm., what was the weight of hydrogen given off by the action of the metal?

14. Air is contained in a closed vessel which has also in it a quantity of water.

If the pressure in the vessel is 760 mm. when the temperature is  $4^{\circ}\text{C}$ ., what would be the pressure when the temperature is  $20^{\circ}\text{C}$ .?

15. A mixture of air and water vapour (unsaturated) is cooled (a) at constant volume, (b) at constant pressure. How does the pressure of the aqueous vapour change in each case; and in which will the temperature at which condensation first occurs be the higher?

16. Describe a method of determining the humidity of the air by direct weighing with a chemical hygrometer.

17. In a chemical hygrometer, air was drawn through drying-tubes into an aspirator. The volume of air which came into the aspirator was 5 litres, the temperature in the aspirator being  $12^{\circ}\text{C}$ . The increase in weight of the drying-tubes was  $\cdot 045$  gm. The temperature of the air outside the apparatus was  $16^{\circ}\text{C}$ . and the barometer reading 750 mm. Calculate the pressure of aqueous vapour in the air, and the relative humidity. (Density of aqueous vapour =  $\cdot 622$  that of air at the same temperature and pressure; weight of a litre of air at  $0^{\circ}\text{C}$ . and 760 mm. =  $1\cdot 293$  gm.)

18. Why are fogs more prevalent in smoky cities than in the open country ?

19. A drop of water is placed in an enclosure initially free from water vapour. How is the rate of evaporation affected by (a) the curvature of the surface of the drops, (b) the purity of the water, (c) the pressure of the air in the enclosure ? How do these three factors affect the final pressure of the vapour if the enclosure is so small that the drop does not completely evaporate ?

## CHAPTER XII

1. In what different ways can heat be transmitted from one place to another ?

Give an example of each process and point out what are its characteristic features.

2. When heat is transmitted by conduction through a sheet of material, upon what factors does the rate of transmission depend ?

3. The thermal conductivity of aluminium in C.G.S. units is  $\cdot 5$ . What quantity of heat would be transmitted per minute through a sheet of aluminium 1 square metre in area and 3 cm. thick if the opposite faces are at temperatures differing by  $30^{\circ}\text{C}$ . ?

4. If the thermal conductivity of aluminium is  $\cdot 5$  in C.G.S. units, what is the conductivity when the unit of heat is the B.Th.U., the unit of length is a foot, and the Fahrenheit scale of temperature is used ? (1 inch =  $2\cdot 54$  cm. ; 1 lb. = 454 gm.)

5. Describe a method of determining the thermal conductivity of a metal like copper.

6. Give an account of the construction and working of a Davy safety lamp, and describe any experiment to illustrate its action.

7. How would you show that water is a very poor conductor of heat ?

8. Why is material like cotton wool such a very poor conductor of heat ?

9. Why does a hot object cool more rapidly when exposed to a draught than it does in still air ?

10. When water is heated in a metal vessel over a flame, the tem-



perature of the outer surface of the vessel is very much lower than that of the flame. Why is this ?

11. A piece of paper is wrapped tightly round a bar, one-half of which is of brass and the other half of wood. The bar is then held over a flame and it is found that the paper is charred where it is in contact with the wood, but not where it is in contact with the brass. Explain clearly how it is that this happens.

12. In the design of boiler furnaces, the problem is not so much to get the heat to flow through the metal of the furnace tube as to get it to flow from the furnace gases to the metal. Illustrate this point by determining what must be the difference in temperature between the two sides of a steel furnace tube 13 mm. thick if the quantity of water evaporated was 200 kilograms per hour per square metre of surface (a very high rate). Take the latent heat of vaporization as 539 calories per gm.; conductivity of steel .11 C.G.S. units.

13. Explain why it is dangerous to allow large deposits of scale to accumulate in boilers.

14. What connection is there between the thermal and electrical conductivities of metals ?

15. How could you compare the thermal conductivities of two metals if they were provided in the form of bars of the same size and shape ?

16. Describe Lee's method of determining the conductivity of poor conductors.

17. Describe a method of determining the conductivity of a liquid.

18. The surface of a pond is in contact with air, at temperature below  $0^{\circ}\text{C}$ ., and ice is forming at the surface. Assuming that the temperature of the air remains constant, and the water is all at  $0^{\circ}\text{C}$ ., find how the rate of increase in thickness of the ice formed varies with the time.

### CHAPTER XIII

1. What do you understand by the statement that heat is transmitted from one place to another by convection ?

Illustrate your answer by describing the action of a system of heating by hot water pipes.

2. Describe the ordinary thermo-syphon system of cooling the engine of a car and explain how it is to some extent self-regulating.

3. Explain the action of a chimney as a means of producing a draught.

4. Explain why a room heated by an open fire is more pleasant and less "stuffy" than one heated by radiators.

5. Describe what you would consider to be a satisfactory method of ventilating a large hall.

6. A chimney is 200 feet high, and the mean temperature of the gases in it is  $250^{\circ}\text{C}$ . Determine the difference in pressure between the inside and the outside of the chimney at a point near the base,

if the temperature and pressure outside are  $15^{\circ}\text{C}$ . and 760 mm. It may be taken that 24 lb. of air pass through the fire for each pound of fuel burnt, and the volume of the products of combustion is about the same as that of the air used, i.e. the density of the flue gases is  $\frac{25}{24}$  that of air at the same temperature and pressure; and the weight of a cubic foot of air at  $0^{\circ}\text{C}$ . and 760 mm. as .08 lb.

## CHAPTER XIV

1. What is meant by the statement that a body is losing heat by radiation ?

Describe any experiments to illustrate the properties of radiation, e.g. how it travels, the way it is reflected and refracted.

2. If two similar thermometers are taken, and the bulb of one is coated with lampblack, it is found that when the two are exposed to sunlight the black-bulb thermometer registers the higher temperature. On the other hand, if the two thermometers are heated and then allowed to cool, the black one cools more rapidly. Explain why this is so, and describe experiments to illustrate your explanation.

3. How is it that on snow-slopes at high elevations one is often very warm in the sunshine while the temperature of the air is much below freezing point and very little melting of the snow occurs ?

4. In gardens, fruit trees, e.g. peaches, are often planted beside a wall which faces south. How does the wall assist their development ?

5. What connection is there between the emissive and absorbing powers of a surface ?

Describe any experiments to illustrate the connection.

6. Describe the construction of a thermopile on some other instrument suitable for detecting and measuring radiation.

7. What reasons have we for supposing that light and the invisible radiation from a hot object are essentially similar ?

8. A hot object, such as a metal vessel or a copper ball at  $200^{\circ}\text{C}$ . or  $300^{\circ}\text{C}$ . (i.e. not nearly hot enough to be luminous), is placed in front of a thermopile. What is the effect of interposing (a) a sheet of glass, (b) a plate of rock salt, (c) a solution of iodine in carbon disulphide contained in a trough of very thin glass ? If an ordinary optical lantern using an arc lamp, and with all its lenses (including the thick condenser) in, be directed on to a thermopile, a considerable effect is produced. How can this fact be reconciled with the results of the experiments of the first part of the Question ?

9. The radiation from an arc lamp differs in quality from that given off from a solid at a temperature of about  $250^{\circ}\text{C}$ . Illustrate what is meant by this statement by considering the behaviour of a narrow beam of the radiation from each of these sources when passed through a prism of rock salt.

10. In the illustration of Question 9, if a prism of glass were used instead of rock salt, what difference would there be in the observed effects ?

11. Describe the construction of a thermos flask and explain why this construction is particularly effective in obtaining heat insulation.
12. Write short notes on the following practical effects:
  - (a) A glass fire screen will cut off a large part of the heating effect of a fire while allowing the fire to be seen.
  - (b) On a sunny day the temperature inside a glass-roofed building, e.g. a greenhouse, is higher than it would be with an opaque roof.
  - (c) A clear night is usually colder than a cloudy one.
13. In an electric incandescent lamp a current is sent through a thin filament which in consequence becomes hot and gives out light. Upon what conditions will the proportion of the electrical energy which is converted to light depend? What becomes of the remainder of the energy? Why can a gas-filled tungsten-filament lamp be made more efficient than a carbon lamp?

## CHAPTER XV

1. Give an account of Prevost's Theory of Exchanges, and explain, in terms of this theory, what happens when a piece of ice is brought near a thermopile in an ordinary room.
2. What do you understand by the "full" radiation corresponding to a particular temperature? Why is the radiation which escapes from a small aperture in a uniform-temperature enclosure taken as equivalent to the radiation from a perfectly black body at that temperature?
3. Experiment shows that the emissive power of a surface is proportional to its absorbing power. Show how this result follows from the theory of exchanges.
4. Radiation of almost any quality passes readily through rock salt, but the radiation from another piece of heated rock salt is strongly absorbed. Show that this is a case of a general result which is to be expected.
5. State Newton's Law of Cooling. To what conditions was Newton referring when he enunciated the law? Under what conditions can it be used to give the rate of cooling of a body sufficiently accurately for practical purposes?
6. State Stefan's Law for the total radiation from a body. In what conditions can it be taken to represent what will actually happen?
7. A body with a dull black surface is placed in an enclosure maintained constantly at  $0^{\circ}\text{C}$ . If conduction and convection are prevented (e.g. by having a very high vacuum in the enclosure), compare the rate of cooling of the body when it is at  $200^{\circ}\text{C}$ . with its rate when it is at  $100^{\circ}\text{C}$ .

## CHAPTER XVI

1. Describe the construction of (a) steel-bulb mercury thermometers, (b) vapour-pressure thermometers, and point out the conditions for which they are suitable.
2. Give an account of the ways in which temperature can be measured electrically.
3. In what way can very low temperatures, e.g.  $-150^{\circ}\text{C}$ . to  $-250^{\circ}\text{C}$ ., be measured?
4. Give an account of the methods available for measuring very high temperatures, e.g.  $2,000^{\circ}\text{C}$ .
5. In what way is the temperature of a body as recorded by a radiation pyrometer affected by the nature of the surface of the body?
6. How are pyrometers calibrated (a) for temperatures up to  $1,600^{\circ}\text{C}$ ., (b) above that temperature? If a pyrometer registers the temperature of a body as  $2,000^{\circ}\text{C}$ ., what precisely does this mean?
7. Give an account of the methods by which the temperature of the sun has been estimated.

## PART II

## CHAPTER XVII

1. Mention some of the chief experimental work which has been done on the relation between the pressure and the volume of a gas and give an account of the nature of the deviations from Boyle's Law observed in the case of gases such as oxygen, nitrogen, and hydrogen, and also of carbon dioxide.
2. Give an account of Andrews' work on the isothermals of carbon dioxide, and show on a rough diagram the shape of the isothermals. By the aid of your diagram explain what is meant by the critical temperature of a substance.
3. If you had available a diagram showing a series of isothermals of a substance, e.g. ether, how would you plot a graph showing the saturated vapour at different temperatures?
4. Discuss the meaning of critical temperature and show how it is possible for a substance to pass without any abrupt change from a state which is undoubtedly gaseous to one which is undoubtedly liquid.

## CHAPTER XVIII

1. Explain clearly how the pressure exerted by a gas is accounted for on the kinetic theory, and show that the theory is consistent with Boyle's Law and Avogadro's Hypothesis.
2. Give an account of Van der Waal's modification of the kinetic



theory so as to include the mutual action of the molecules and their finite dimensions. Show that this modification is consistent with the observed deviations from Boyle's Law. Show how the constants in Van der Waal's equation are connected with the critical constants of a substance and hence how an indication of the critical temperature of a gas can be deduced from observations of its deviation from Boyle's Law.

## CHAPTER XIX

1. Describe a method of determining the specific heat of a gas (*a*) at constant volume, (*b*) at constant pressure. Why is the latter specific heat necessarily greater than the former?

2. In some stationary steam-engine plants, the feed-water for the boiler is heated by causing it to flow through tubes over which the gases from the furnaces pass on their way to the chimney, the arrangement constituting an "economizer." Assuming that the flue gases reach the economizer at a temperature of 350° C. and leave it at 200° C., calculate the amount of heat saved per pound of coal. Take the specific heat at constant pressure of the flue gases as .21; that 75 per cent. of the heat from the gases goes into the water; that for each pound of coal 24 lb. of air are used, so that 25 lb. of flue gases are formed. Express the result as a percentage of the calorific value of the coal, which is 8,000 T.U. per pound.

3. Give an account of experiments to determine whether any internal work is done when a gas expands, and describe the results obtained.

4. In the Joule and Thomson porous-plug experiment a heating effect was obtained with hydrogen. Explain clearly what this indicates.

5. Describe in outline the modern method of liquefying air by the regenerative cooling method.

6. Describe the method of liquefying hydrogen and point out why the arrangement used in the case of air must be modified for hydrogen and helium and in what the modification consists.

## CHAPTER XX

1. What is meant by an adiabatic change? Show that if a certain quantity of gas increases its volume by a given amount, the fall in pressure will be greater for an adiabatic change than for an isothermal one.

2. What is meant by a "perfect" gas?

If  $pV = RT$  is the general equation for a perfect gas, show that (a)  $J(C_p - C_v) = R$  where  $C_p$  and  $C_v$  are the thermal capacities of the gas at constant pressure and volume respectively. (b) The equation for an adiabatic change is  $pV^\gamma = \text{constant}$  where  $\gamma = C_p/C_v$ .

3. In a Diesel engine, air alone is taken into the cylinder on the induction stroke and is compressed on the next stroke. The temperature is raised so much by the compression that when the fuel is sprayed



in it automatically ignites. Assuming that air is taken into a Diesel cylinder at  $27^{\circ}$  C. and 15 lb. per square inch and is compressed adiabatically until at the top of the stroke the pressure is 500 lb. per square inch, calculate (a) the compression ratio, i.e. the ratio of the volume available for the air, when the piston is at the end of its outstroke, to the volume when the piston is at the end of its instroke; (b) the temperature of the air at maximum compression.

4. The volume elasticity of a substance is defined as the ratio of the increase in pressure  $\delta p$  to the corresponding strain  $-\frac{\delta v}{v}$  for compression. Show that the elasticity of a gas for an adiabatic compression is equal to  $\gamma p$ . Take  $\gamma$  as 1.40.

Hence show how the value of  $\gamma$  may be deduced from a determination of the velocity of sound in a gas.

5. Give an account of the methods of determining  $\gamma$ .

How does a knowledge of  $\gamma$  give an idea of the number of atoms in the molecule of the gas?

## CHAPTER XXI

1. What is meant by an indicator diagram for an engine and what information does it give?

2. What is the First Law of Thermodynamics? What is the essential condition in order that heat may be continuously converted to work by a heat engine?

3. What is meant by a reversible cycle?

Describe Carnot's cycle; upon what does the efficiency of this cycle depend?

4. Show that for engines working between the same temperatures no engine can be more efficient than one working on a reversible cycle. How does this proposition lead to the idea of a scale of temperature independent of the properties of any substance?

5. Explain how the absolute thermodynamic scale of temperature is defined, and show that it coincides with the perfect gas scale.

## CHAPTER XXII

1. Give an account of the Principle of the Conservation of Energy and the Principle of the Dissipation and Degradation of Energy.

2. What is meant by the entropy of a substance? Show that the entropy of a substance in a certain state depends only on that state and not on the way it was reached. Calculate the entropy of a pound of saturated steam at  $100^{\circ}$  C. and 760 mm., taking the entropy of water at  $0^{\circ}$  C. and 760 mm. as zero.

3. If the working substance in an engine is taking in heat from a source at a temperature  $\theta$ , and if we know that the entropy of the substance in the initial and final states is respectively  $\phi_1$  and  $\phi_2$ , what does this tell us about the amount of heat absorbed by the substance? Explain carefully what your statement means.

## ANSWERS

## CHAPTER II

6.  $36.9^{\circ}\text{C.}$ ;  $176.7^{\circ}\text{C.}$ ;  $-12.2^{\circ}\text{C.}$ ;  $-23.3^{\circ}\text{C.}$ ;  $25^{\circ}\text{C.}$  7.  $59^{\circ}\text{F.}$ ;  $5^{\circ}\text{F.}$ ;  $-459.4^{\circ}\text{F.}$ ;  $54.5^{\circ}\text{F.}$

## CHAPTER III

1. About 3.89 inches. 2. 1.00038 metres. 3. 40.51 cm. 4. 0.136 inches. 5. Expansion of the steel calipers themselves for a range of  $20^{\circ}\text{C.}$  would make a difference of .0022 cm., i.e. about  $\frac{1}{50}$  mm. on a 10 cm. length. Thus maximum uncertainty would be of the order of the degree of accuracy of the reading and it would hardly be worth correcting for the expansion of the scale. 8. 5.448 tons weight. 9. Not less than  $464^{\circ}\text{C.}$  10. (a) 3.25079 cm. (b) 3.24943 cm.

## CHAPTER V

2. .000159. 3. .00107 (range  $0^{\circ}\text{C.}$  to  $50^{\circ}$ ). 5. .0000235. 6. .0000015. 7. (a) .82 per cent., (b) .28 per cent. 10. .00110 (range  $0^{\circ}$ – $30^{\circ}\text{C.}$ ). 13. .000181. 14. An error of .01 cm. represents .84 per cent. of 1.18 cm. and therefore .84 per cent. of the result. Expansion of silica represents .82 per cent. of expansion of mercury (Question 7). Hence reading of difference of heights must be correct to at least .01 cm. 15. 75.313 cm.

## CHAPTER VI

1.  $\frac{1}{8}$  cubic foot or 288 cubic inches. 2.  $6\frac{3}{8}$  cubic feet less  $\frac{1}{8}$  cubic foot which would still be in when the pressure became atmospheric. 4. 75.45 cm. 7. 77.6 lb. per square inch. 8. .00366. 11.  $58.1^{\circ}\text{C.}$  13. (a)  $-273^{\circ}\text{C.}$ , (b)  $-459.4^{\circ}\text{F.}$  14. 419.6 c.c. 15. .005309 lb. 16. 1,128 gm.

## CHAPTER VII

2. 1.73 pence nearly. 3. 300 calories; 22.2 calories. 5. 7,893 calories per gm. 7. .0305. 9. .51. 10.  $1205^{\circ}\text{C.}$  (i.e. about  $1200^{\circ}\text{C.}$ ). 12. .52.

## CHAPTER VIII

3. 10 B.H.P. (9.991). 8. 10.63 T.U.; 14,810 foot lb.;  $J = 1,393$  foot lb. per T.U. [Note.—There is an uncertainty in the cooling correction depending on the graph which might be as much as  $.15^{\circ}\text{C.}$ , making an uncertainty of about 1 per cent. in the result.] 9. About .2 (1964). 10. About 136 lb. weight. 11. 13.57 per cent. 13. Heat developed at the rate of over 235,000 T.U. per minute. 14. 2,325 foot lb.; 1.661 T.U. 15. (a) 1.482 T.U., (b) .109 T.U. The total differs from 1.661 by .07 T.U., the equivalent of the energy of a bullet moving at 500 feet per sec. 17. (a) 1400.4, (b)  $4.187 \times 10^7$ , (c) 426.8. 20. Twenty and a half minutes.

## CHAPTER IX

5. 29,344 calories. 6. 57.7 gm. ; the temperature would be reduced to 0° C. and about 30 gm. of ice left unmelted. 13. .49.

## CHAPTER X

4. 38.1° C. 5. 75.28 per cent. 6. 575 T.U. ; 38.3 lb. of cooling water. 22. .21.

## CHAPTER XI

7. .59 nearly. 8. The warm day would feel to be the drier, but the amount of water vapour per unit volume would be greater than on the cold day. 12. 746 mm. of mercury. 13. .04241 gm. 14. 815 mm. 15. Temperature higher in case (b). 17. 8.9 mm. (8.896) ; Rel. Humidity .654.

## CHAPTER XII

3. Three million calories. 4. .0336 B.Th.U. per square foot per 1° F. per foot temperature gradient. 12. 35.4° C. 18. Rate of formation of ice  $\propto$  rate of flow of heat through ice sheet and since temperature difference between faces of ice sheet is constant, the temperature gradient  $\propto \frac{1}{x}$ . Thus  $\frac{dx}{dT} = K \cdot \frac{1}{x} \therefore \frac{dx}{dT} \propto \frac{1}{\sqrt{T+c}}$  where

T is the time, and c a constant depending on the moment from which T is measured.

## CHAPTER XIII

6. 6.47 lb. per square foot.

## CHAPTER XV

7. Rate of cooling at 200 C. = 3.225 times that at 100° C.

## PART II

## CHAPTER XIX

2. 7.4 per cent.

## CHAPTER XX

3. (a) 12.25, (b) 544° C.

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